SYNTHESIS AND THERMAL DECOMPOSITION OF SOME BIS (2-THENOYL) PEROXIDES

Thesis for the Degree of Ph. D.

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Daniel Myron Teller

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This is to certify that the

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of Some Bis(2-Thenoyl) Peroxides

presented by

Daniel Myron Teller

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SYNTHESIS AND THERMAL DECOMPOSITION
OF SOME BIS(2-THENOYL)PEROXIDES

By

Daniel Myron Teller

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* * * * * * * *

To my wife, Madelyn

VITA

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ABSTRACT

The effect of substituents on the rate of spontaneous thermal decomposition of substituted bis(2-thenoyl)peroxides in carbon tetrachloride has been investigated. A new series of symmetrical 5,5'-disubstituted bis(2-thenoyl)peroxides was prepared, in which the substituents were chloro, bromo, methyl, _t_-butyl and nitro groups. Two new 4,4'-disubstituted bis(2-thenoyl)peroxides, the 4,4'-dimethyl and 4,4'-dibromo compounds were also studied, as well as the unsymmetrical 5-methyl bis(2-thenoyl)peroxide. Although it is not structurally a bis(2-thenoyl)peroxide, bis(3-thenoyl)peroxide was prepared and studied for comparative purposes.

The rates of the spontaneous decomposition of these peroxides were determined by carrying out their decompositions in the presence of an efficient free-radical scavenger. The scavenger trapped the radicals formed in the spontaneous decomposition, thus preventing any induced decomposition of unreacted peroxide by attack of the initially-formed radicals. All of the decompositions were carried out in dilute solutions of carbon tetrachloride. The scavenger used was 3,4-dichlorostyrene. In all cases studied with the exception of bis(5-nitro-2-thenoyl) peroxide, the rates of thermal decomposition followed strict first order kinetics. The first

order rate constants for the decomposition of the peroxides in carbon tetrachloride in the presence of 3,4-dichlorostyrene, determined at 75° are:

Peroxide	$k \times 10^3$ (min.$^{-1}$)
Bis(5-methyl-2-thenoyl)	2.54
Bis(5-_t_-butyl-2-thenoyl)	2.43
5-Methyl bis(2-thenoyl)	1.79
Bis(4-methyl-2-thenoyl)	1.76
Bis(2-thenoyl)	1.33
Bis(3-thenoyl)	1.29
Bis(5-chloro-2-thenoyl)	0.95
Bis(5-bromo-2-thenoyl)	0.92
Bis(4-bromo-2-thenoyl)	0.69

Examination of the rate constants shows that the presence of electron donating substituents on the thiophene ring accelerates the rate of decomposition, while electron drawing substituents have the opposite effect.

A close parallel in rate constants is observed, both in the absolute values and the relative order for the corresponding thenoyl and benzoyl peroxides, if the reasonable assumption is made that the 5-substituted 2-thenoyl peroxides are analogous to the para-substituted benzoyl peroxides, and the 4-substituted 2-thenoyl peroxides are analogous to the meta-substituted benzoyl peroxides.

When the values of log k/k_0 were plotted against the sum of the σ values for the substituents, a reasonably good straight line resulted, which had a ρ value of -0.44. Thus it was demonstrated that the Hammett equation is applicable to the spontaneous decomposition of the substituted bis(2-thenoyl) peroxides.

The activation energies were obtained from the rate constants determined at three different temperatures, and were found to be 29.5 - 1.0 kilocalories per mole for all of the peroxides studied. The fact that the rate constants show a definite dependence on the electronic character of the particular substituent, while the activation energies are relatively constant over the entire range of substituents, indicates that the frequency factor must vary with a change in substituent, and thus the Hammett relationship can only be approximate when applied to an interpretation of the rates of decomposition of the substituted bis(2-thenoyl) peroxides.

TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF TABLES - Continued

LIST OF TABLES - Continued

LIST OF FIGURES

LIST OF FIGURES - Continued

LIST OF FIGURES - Continued

LIST OF FIGURES - Continued

INTRODUCTION

The effect of structural changes in organic molecules on their rate of non-radical reactions has been rather thoroughly investigated (1,2). In the reactions of meta and para-substituted benzene derivatives, such investigations have shown that for a wide variety of substituents the effect on the reactivity of a given benzene derivative is determined by the polar effect of a particular substituent. The quantitative relationship between the effect of the substituent and the rate of reaction is embodied in the Hammett equation for meta and para-substituted benzene derivatives (3),

$$\log k/k_o = \sigma\rho$$

The term log k/k_o represents the logarithm of the ratio of the rate constant of the substituted compound, k, to the rate constant of the unsubstituted compound, k_o. The reaction constant, ρ, is a measure of the susceptability of a given reaction to polar effects produced by the substituents. The substituent constant, σ, is a measure of the ability of a given substituent to change the electron density at the reaction center.

The first successful application of the Hammett equation to a unimolecular free-radical reaction was reported (4) in a study of the effect of substituents on the rate of the spontaneous thermal decomposition of a series of meta and para-substituted benzoyl peroxides.

In view of this work it seemed of interest to study a series of substituted bis(2-thenoyl) peroxides, to determine whether the Hammett equation would be applicable to the spontaneous thermal decomposition of such a series of compounds. If this were the case, then it should be possible to draw a correlation between the corresponding benzoyl and thenoyl peroxides.

HISTORICAL

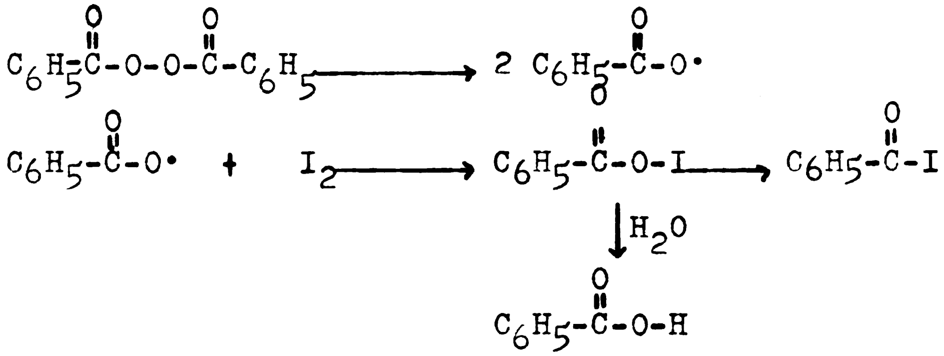
Diacyl peroxides are relatively unstable compounds, which can be decomposed either thermally or photochemically.

There is good experimental evidence that such decompositions proceed by a free-radical mechanism. The decomposition of acetyl peroxide is catalyzed by ultra-violet light (5). The rate of decomposition of benzoyl peroxide is accelerated by the presence of free-radicals.(6). When benzoyl peroxide is decomposed in substituted benzene solvents, substitution of peroxide fragments occurs in the ortho and para position of the solvent molecules, regardless of the directive influence of the substituent (7). Perhaps of greater significance is the fact that certain substances, which are known to inhibit free-radical chain reactions, will lower the overall rate of decomposition of benzoyl peroxide (6).

The initial cleavage in the decomposition of diacyl peroxides is, at present, thought to occur at the oxygen-oxygen bond,

$$R-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-R \xrightarrow{\qquad\qquad} 2\ R-\overset{O}{\overset{\|}{C}}-O\bullet$$

Convincing evidence for this mode of cleavage, in the case of benzoyl peroxide, was obtained by Hammond and Soffer (8). They decomposed benzoyl peroxide in anhydrous carbon tetrachloride, in the presence of a very efficient free-radical inhibitor, iodine, and isolated iodobenzene in 90% yield, However, when the decomposition was carried out in moist carbon tetrachloride in the presence of iodine, an almost quantitative yield of benzoic acid was obtained. They proposed the following sequence of reactions to account for these products,



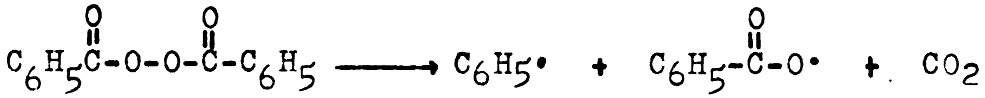
$$C_6H_5\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-C_6H_5 \longrightarrow 2\ C_6H_5-\overset{O}{\overset{\|}{C}}-O\cdot$$

$$C_6H_5-\overset{O}{\overset{\|}{C}}-O\cdot \ + \ I_2 \longrightarrow C_6H_5-\overset{O}{\overset{\|}{C}}-O-I \longrightarrow C_6H_5-\overset{O}{\overset{\|}{C}}-I$$

$$\downarrow H_2O$$

$$C_6H_5-\overset{O}{\overset{\|}{C}}-O-H$$

Benzoyl hypoiodite is thought to decompose under anhydrous conditions to form iodobenzene, and in the presence of water would hydrolyze rapidly to yield benzoic acid. Thus the initial cleavage of benzoyl peroxide must produce intact benzoate radicals quantitatively. This evidence more or less precludes the mechanism postulated by Nozaki and Bartlett (6) in which the initial cleavage of benzoyl peroxide yielded a molecule of carbon dioxide, a benzoate radical and a phenyl radical.



$$C_6H_5\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-C_6H_5 \longrightarrow C_6H_5\cdot \ + \ C_6H_5-\overset{O}{\overset{\|}{C}}-O\cdot \ + \ CO_2$$

However, the decomposition of benzoyl peroxide does not obey a first-order kinetic rate expression which it would be expected to do if the spontaneous cleavage proposed by Hammond and Soffer were the only decomposition process taking place. The overall rate of decomposition of the peroxide is greater than first-order to an extent which varies widely with the solvent. Thus, another mode of decomposition must be superimposed upon the spontaneous decomposition. This induced decomposition is thought to involve a chain reaction in which the initially formed radicals attack benzoyl peroxide molecules to produce further decomposition, or alternatively, the initially formed radicals may attack solvent molecules to form solvent radicals which are in turn capable of attacking benzoyl peroxide molecules. These views on the overall decomposition path were put forth independently by Bartlett and Nozaki (6,9) and by Cass (10), who derived mathematical expressions for obtaining the rate constant for the spontaneous decomposition from the experimental data on the overall decomposition rate.

More recently, Swain, Stockmayer and Clarke (4) have employed free-radical inhibitors to completely repress the induced decomposition of benzoyl peroxides, thereby making the observed rate of decomposition equivalent to the rate of their spontaneous decomposition. Several vinyl monomers were found to be efficient inhibitors of the induced decomposition. However, from such studies, for a series of para and meta-substituted benzoyl peroxides in various solvents, it was concluded that 3,4-dichlorostyrene was the most generally effective inhibitor. Employing the inhibitor method with substituted benzoyl peroxides, these investigators found that the rate of spontaneous decomposition was increased by electronrepelling substituents and decreased by electron-attracting substituents. The rate constants for the spontaneous decomposition of sixteen para and meta-substituted benzoyl peroxides were found to fit the Hammett equation (page 1) reasonably well. This was the first case of a successful application of the Hammett relationship to a unimolecular free-radical process.

Blomquist and Buselli (11) made a similar and independent study of the spontaneous decomposition of substituted benzoyl peroxide. They found that the induced decomposition could be eliminated by using acetophenone as a solvent. Their results are in good agreement with those of Swain, Stockmayer and Clarke (4). However, they found that both the activation energy and the frequency factor were affected in a systematic manner by the substituents. Since the Hammett relationship is exact only for those reactions in which the frequency factor is unaffected by a change of substituents, the Hammett equation is only approximate for substituted benzoyl peroxide.

Diaroyl peroxide are, in general, prepared by the reaction of an acid chloride with sodium peroxide at 0° (12). Substituted benzoyl peroxides (13) are readily prepared by the addition of the acid chloride, dissolved in toluene or cyclohexane, to a chilled aqueous solution of sodium peroxide. The peroxide precipitates from the reaction mixture in a high state of purity.

Breitenbach and Karlinger (14) prepared bis(2-thenoyl) peroxide, the only thenoyl peroxide reported, prior to the present investigation, by the action of hydrogen peroxide on 2-thenoyl chloride in the presence of pyridine. These investigators used this peroxide as a free-radical initiator in the polymerization of styrene. By analyzing the resulting polymer for sulfur, they were able to determine the fate of the peroxide initiator.

Recently, Ford and Mackay (15) made a detailed study of the products of the decomposition of bis(2-thenoyl) peroxide in a variety of aromatic solvents. They found that very little carbon dioxide was evolved and that the products formed could be attributed largely to reactions of the thenoate free-radical, apparently due to the high degree of resonance stabilization of this radical. This is in distinct contrast to the decomposition of benzoyl peroxide, in which carbon dioxide is evolved in high yields (16). When benzene, nitrobenzene, chlorobenzene, bromobenzene and iodobenzene were used as reaction media, the products of the decomposition of bis(2-thenoyl) peroxide consisted of large amounts of unidentified, amorphous sulfur-containing material, moderate amounts of 2-thenoic acid and small amounts of simple neutral products. The simple neutral products included aryl 2-thenoates formed by nuclear attack of thenoate radicals on the solvent, and in the case of the halo benzenes, phenyl 2-thenoates formed by the displacement of the halogen atom, as well as the para-substituted esters. Presumably, the 2-thenoic acid arises through a hydrogen abstraction by the 2-thenoate radicals, involving the accumulating amorphous, sulfur containing material. When toluene and especially cumene were used as reaction solvents, the availability of active hydrogen atoms in the side-chains lead to hydrogen abstraction from the solvent, with the formation of large amounts of dibenzyl and dicumyl, respectively, and no amorphous material. In cumene the yield of 2-thenoic acid was quantitative, and dicumyl was the only neutral product isolated, indicating exclusive side-chain hydrogen abstraction. In toluene, dibenzyl was the major neutral product, but small quantities of tolyl-2-thenoates and 2-benzyl thiophene were also isolated.

The formation of small amounts of 2-benzyl thiophene in the decomposition of bis(2-thenoyl) peroxide in toluene, together with the observation that its decomposition in thiophene as a solvent produced some 2,2'-dithienyl was offered as evidence for the generation of 2-thienyl free-radicals. However, the low yields of these products together with the scanty evolution of carbon dioxide seem to substantiate the hypothesis that 2-thenoate free-radicals are rather stable and undergo decarboxylation to only a limited extent.

EXPERIMENTAL

Chemical Reagents and Apparatus

The carbon tetrachloride used as the solvent in the kinetic studies and product analyses was purified by heating two liters of C.P. grade carbon tetrachloride at 60°, for one-half hour, with a caustic solution prepared from 20 g. of potassium hydroxide, 150 ml. of ethyl alcohol and 150 ml. of water. This treatment was repeated and the carbon tetrachloride layer was separated and washed thoroughly with water to remove the ethyl alcohol. It was then shaken with small portions of concentrated sulfuric acid until the acid layer no longer showed any color. It was finally washed with water to remove the sulfuric acid, dried over anhydrous calcium chloride, and distilled from phosphorous pentoxide through a 12" glass helix packed column.

The styrene, used as a radical trap in the kinetic studies, was Eastman Kodak Co., White Label material, stabilized with t-butylcatechol. It was distilled in a nitrogen atmosphere under reduced pressure, just prior to use. Its properties were, b.p. 50° (25 mm.), n_D^{20} 1.5462. Literature values (17), b.p. 46° (20 mm.), n_D^{20} 1.5462. The styrene was stored in the refrigerator without the addition of an inhibitor.

The 3,4-dichlorostyrene used as a radical trap, in the kinetic studies and carbon dioxide determinations was synthesized as described in a later section of this thesis (see page 46). It was stored in the refrigerator without the addition of an inhibitor. Under these conditions polymerization did not occur, as evidenced by the fact that the refractive index was unchanged after a storage period of two months. By comparison, the refractive index of the dichlorostyrene decreased from n_D^{20} 1.5844 to n_D^{20} 1.5838 after allowing it to stand at 25° for ten hours.

The N-bromosuccinimide used in the preparation of 3-thenyl bromide was obtained from Mathieson and Co., and was recrystallized from glacial acetic acid just prior to use. The α,α'-azodiisobutyronitrile, a free-radical source used in the same preparation, was obtained from Eastman Kodak Co., as their White Label product.

The toluene, cyclohexane and benzene used in the preparation of the bis(2-thenoyl) peroxides were of C.P. grade, and were dried over metallic sodium.

The 3-methylthiophene was obtained from the Socony-Mobil Oil Company as a research sample and was distilled just prior to use.

The 2-bromothiophene was obtained from the Michigan Chemical Corporation as a research sample and was distilled just prior to use. The 2-chlorothiophene was obtained from the same source and was used without further purification.

Thiophene was purchased from the Pennsalt Chemicals Corporation.

Thionyl chloride, practical grade, was purchased from the Eastman Kodak Company and was used as received, unless otherwise specified in the section of this thesis entitled, "Syntheses".

Dimethyl formamide was purchased from the Eastman Kodak Company, as their White Label product.

Phosphorous oxychloride was purchased from the Baker Company, as their Analyzed Reagent product.

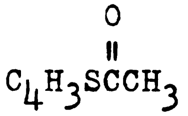
Sodium peroxide was purchased from the Mallinkrodt Company, as their Analytical Reagent product.

All melting points were determined using capillary tubes, in an electrically heated, mechanically stirred silicone oil bath, and are uncorrected.

The microelementary analyses were performed by the Micro-Tech Laboratories, Skokie, Illinois.

Syntheses

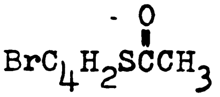
2-Acetylthiophene



$C_4H_3S\overset{\overset{O}{\|}}{C}CH_3$

The method of Hartough and Kosak (18) was used in this preparation. A solution of 252 g. (3.0 moles) of thiophene and 117 g. (1.1 moles) of 95% acetic anhydride was heated to 70° in a one-liter three-necked flask fitted with a reflux condenser, dropping funnel, stirrer, and thermometer. With vigorous stirring, 10 g. of 85% orthophosphoric acid was added over a period of ten minutes. A slight rise in temperature occurred after the addition of the orthophosphoric acid was begun and cooling with an ice-bath became necessary towards the end of the addition of the catalyst to maintain the reaction temperature below 90°. The reaction solution was then refluxed at 96° for two hours and allowed to cool to 50°. A volume of 200 ml. of water was added and the solution was stirred for another 15 minutes. The organic layer was separated and washed with 200 ml. of 10% sodium carbonate solution, followed by washing with 200 ml. of water. The thiophene-water azeotrope was removed by distillation at 68°, followed by excess thiophene distilling at 84°. Vacuum distillation of the residue through an 8" Vigreux column gave 120 g. (0.95 mole, 95%) of colorless 2-acetylthiophene boiling at 75° (2 mm.). Literature value, (18) b.p. 77° (4 mm.).

5-Bromo-2-acetylthiophene

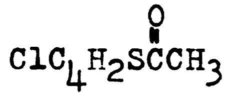


$BrC_4H_2S\overset{O}{\overset{\|}{C}}CH_3$

Using the apparatus and general procedure described above, 81 g. (0.5 mole) of 2-bromothiophene and 59.2 g. (0.58 mole) of analytical grade acetic anhydride were heated to 80°. Heating was discontinued and 5 g. of 85% orthophosphoric acid were added dropwise, during which time the reaction temperature rose to 82°. The solution was heated at 100-110° for three hours, during which time it darkened to a red-black color. Upon cooling to room temperature the material solidified. The solid was melted by heating with a microburner, 100 ml. of water were added and the mixture was stirred for another 15

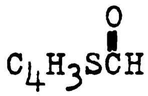
minutes. The resulting brown solid was filtered, washed with 100 ml. of 10% sodium carbonate solution, and then with water. The yield of crude product after drying was 77 g. (0.375 mole, 75%) melting at 90-92°. Literature value (19), m.p. 94-95°. Recrystallization of the crude product from ethyl alcohol yielded 59 g. of light yellow colored crystals melting at 90-92°. An additional 9 g. of product was obtained by adding water to the mother liquor.

5-Chloro-2-acetylthiophene


$ClC_4H_2S\overset{O}{\overset{\|}{C}}CH_3$

Using the apparatus and general procedure described above, 108 g. (0.91 mole) of 2-chlorothiophene, and 118 g. (1.15 moles) of analytical grade acetic anhydride were heated to 75°. Upon careful addition of 10 g. of 85% orthophosphoric acid, there was no rise in the reaction temperature. The reaction solution was heated at 100-110° for two hours, during which time it darkened and finally turned black in color. The reaction solution was allowed to cool to room temperature and 100 ml. of water were added. The organic layer was separated, washed twice with water, then with 10% sodium carbonate solution until neutral to pHydrion paper, and finally twice with water. The black colored solution was distilled *in vacuo* to give 102 g. (0.638 mole, 70%) of light yellow colored liquid boiling at 88° (4 mm.). Literature value (18), b.p. 88° (4 mm.). Recrystallization from cyclohexane gave 87 g. of colorless needles melting at 45.5-46.5°. Literature value (18), m.p. 46.5-47°.

2-Thenal



$C_4H_3S\overset{\overset{O}{\|}}{C}H$

The method of Campaign and Archer (20) was employed in this preparation. A solution of 126 g. (1.5 moles) of thiophene and 138 g. (1.92 moles) of dimethyl formamide contained in a one-liter three-necked flask fitted with an Allihn condenser (protected by a calcium chloride tube), stirrer and dropping funnel was cooled to 0°. With stirring, 288 g. (1.86 moles) of phosphorous oxychloride were added at 0° over a period of one hour. The reaction mixture was heated on the steam bath for two hours, during which time it darkened and finally became black in color. After being set aside at room temperature overnight, the reaction solution was poured with stirring, into a beaker containing 1500 g. of ice. A volume of 300 ml. of a saturated solution of sodium acetate was added. The heavy oily layer was separated, and the aqueous layer was extracted with 300 ml. of ethyl ether. The combined oily layer and ether extracts were washed free of acid with 10% sodium bicarbonate solution, then washed with water, and dried over anhydrous calcium chloride. The ether was removed by distillation on a steam bath and the red oily residue was distilled <u>in vacuo</u> through an 8" Vigreux column to yield 133 g. (1.19 moles, 79%) of a colorless liquid boiling at 54° (3 mm.). Literature value (20), b.p. 44-45° (1.1 mm.).

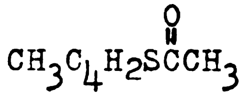
2-Methyl thiophene $C_4H_3SCH_3$

The experimental procedure of King and Nord (21) was followed to obtain this compound. A solution containing 112 g. (1.0 mole) of 2-thenal, 200 ml. (4.0 moles) of 85% hydrazine hydrate and 800 ml. of ethylene glycol was stirred in a two-liter three-necked flask fitted with a stirrer, thermometer and Vigreux column equipped with a distillation head. The solution was heated at 130-160° to distill excess hydrazine and water. The residue was cooled to 50°, the Vigreux column was replaced by an Allihn condenser, 200 g. of potassium hydroxide pellets were added, and heating was resumed. At about 90° the evolution of nitrogen commenced. The reaction mixture was stirred with heating for another 12 hours. The condenser was replaced by a Vigreux column and distilling head, and the distillate boiling up to 150° at atmospheric pressure was collected. The distillate was extracted with several portions of ethyl ether, which were combined, washed with 6 N hydrochloric acid and finally washed with water. After drying over anhydrous calcium chloride, the ether was removed by distillation on a steam bath. Distillation of the residue through an 8" Vigreux column gave a total of 63 g. (0.64 mole, 64%) of colorless 2-methyl thiophene boiling at 110-110.5° (1 atm.). Literature value (21), b.p. 112-113° (1 atm.).

2-*t*-Butyl thiophene $C_4H_3SC(CH_3)_3$

The general experimental procedure of Caesar (22) was followed in the preparation of the alkylthiophene. A solution prepared from 168 g. (2.0 moles) of thiophene and 15 g. of 75% sulfuric acid, contained in a one-liter three-necked flask fitted with a stirrer, reflux condenser, thermometer and a sintered glass gas inlet tube, was heated to 70°. Gaseous isobutylene (116 g., 12.1 moles) was introduced into the well-stirred reaction solution through the gas inlet tube at a rate sufficient to maintain the reaction temperature at 60-70°. The addition of the alkene required four hours. After allowing the reaction mixture to come to room temperature, the organic layer was separated, washed with 10% sodium hydroxide solution until the washings were basic to pHydrion paper, then washed with water, after which it was dried over anhydrous calcium chloride. Distillation at atmospheric pressure through a 12" glass helix packed column yielded 153 g. (1.09 moles, 54.6%) of product. Its physical properties are, b.p. 160-166°, n_D^{20} 1.4983. Literature values (23), b.p. 163.9, n_D^{20} 1.4979.

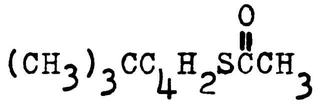
5-Methyl-2-acetylthiophene



$CH_3C_4H_2S\overset{\overset{O}{\|}}{C}CH_3$

The apparatus and general procedure described in the preparation of 2-acetylthiophene were used to obtain this material. A total of 5 g. of orthophosphoric acid were added. dropwise, at room temperature, to a stirred solution of 49 g. (0.5 mole) of 2-methyl thiophene and 55 g. (0.54 mole) of reagent grade acetic anhydride. The reaction temperature rose to 40° during the addition of the acid catalyst, after which the solution was heated at 100-110° for three hours. After cooling the reaction mixture, adding water and stirring for 15 minutes, the organic layer was separated and washed with 10% sodium carbonate solution. The dark brown colored crude product was dried over anhydrous magnesium sulfate and distilled through an 8" Vigreux column *in vacuo*. The yield was 40 g. (0.285 mole, 57%) of clear liquid boiling at 84° (3 mm.). Literature value (18), b.p. 84.5° (3 mm.).

5-*t*-Butyl-2-acetylthiophene



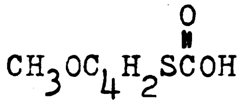
$(CH_3)_3CC_4H_2S\overset{\overset{O}{\|}}{C}CH_3$

The apparatus and general procedure described in the preparation of 2-acetylthiophene were used to obtain this product. A total of 5 g. of orthophosphoric acid were added dropwise, at room temperature, to a stirred solution of 70 g. (0.50 mole) of 2-*t*-butyl thiophene and 58 g. (0.527 mole) of practical grade acetic anhydride. The reaction temperature rose to 35° during the addition of the acid catalyst. The stirred reaction solution was heated at 80-90° for one and three-quarter hours, cooled to 50°, and water was added. The resulting solution was set aside at room temperature overnight. A 50 ml. volume of ethyl ether was added to dissolve the milky suspension which had formed. The organic layer was separated, washed with 10% sodium carbonate solution, then washed with water, and dried over anhydrous magnesium sulfate. Vacuum distillation through an 8" Vigreux column yielded a fore-run of 12 g. of unreacted 2-t-butyl thiophene, b.p. 35-40° (2 mm.), and 2 g. of a liquid, b.p. 80-100° (2 mm.), followed by 66 g. (0.362 mole, 72%) of a clear liquid product boiling at 100-101.5° (2 mm.), n_D^{20} 1.5347. Literature values (23), b.p. 114° (4 mm.), n_D^{20} 1.5343.

2-Methoxythiophene $C_4H_3SOCH_3$

The experimental procedure of Sicé (24) was followed in the preparation of this compound. A solution prepared by dissolving 19.8 g. (0.86 g.at.) of sodium in 225 g. of absolute methanol was contained in a one-liter three-necked flask fitted with a stirrer and reflux condenser. The quantities, 45.6 g. (0.28 mole) of 2-bromothiophene, 11.4 g. of pulverized cupric oxide and 0.2 g. of sodium iodide were added to the solution at room temperature. The stirred mixture was refluxed for 87 hours. After it had cooled to room temperature, the reaction mixture was filtered and the filtrate was poured into 600 ml. of cold water. The resulting solution was set aside overnight and extracted with ethyl ether. The combined ether extracts were washed with water, dried over anhydrous magnesium sulfate and the ether removed by distillation on a steam bath. The residue was distilled <u>in vacuo</u> from sodium through an 8" Vigreux column to give 20.5 g. (0.18 mole, 64%) of clear liquid product boiling at 34-35° (4 mm.). Literature value (24), b.p. 74-75° (50 mm.).

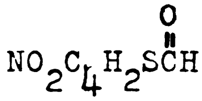
5-Methoxy-2-thenoic acid



$\mathrm{CH_3OC_4H_2S\overset{\overset{O}{\|}}{C}OH}$

The experimental procedure of Sicé (24) was used to obtain this acid. A 2.8 g. (0.248 g.at.) quantity of lithium, cut into pieces of approximately 2 cm.^{3}, was added to 20 ml. of anhydrous ethyl ether contained in a 300-ml. three-necked flask fitted with an Allihn condenser, stirrer, dropping funnel and nitrogen inlet-tube. The reaction was carried out in an atmosphere of dry nitrogen. A solution containing 21.7 g. (0.138 mole) of dry bromobenzene dissolved in 80 ml. of anhydrous ethyl ether was added dropwise to the stirred suspension of lithium in ether, over a period of approximately 30 minutes. The rate of addition was sufficient to cause the reaction solution to reflux gently. Stirring was continued for 30 minutes after the addition of bromobenzene was completed, at which time refluxing had ceased. A solution of 24 g. (0.211 mole) of 2-methoxythiophene dissolved in 80 ml. of anhydrous ethyl ether was added dropwise to the stirred reaction mixture, over a period of 45 minutes. The resulting mixture was heated on a steam bath for one hour, cooled to room temperature, and poured into a three-liter beaker containing a slurry of 300 g. of crushed dry ice in anhydrous ethyl ether. After standing at room temperature for two and one-half hours, 200 ml. of water were added dropwise to the stirred reaction mixture, while maintaining the temperature at 0°, by means of an ice bath. The hydrolyzed reaction mixture was stirred for two hours following the addition of the water, to remove any unreacted lithium. The water layer was separated. The ether layer was extracted with three 100 ml. portions of 10% sodium hydroxide solution and the basic extracts were added to the water layer. The combined aqueous layer and basic extracts were washed with two 100 ml. portions of ethyl ether, cooled to room temperature, filtered, and acidified with concentrated hydrochloric acid. The resulting precipitate was recovered by filtration, washed with water and air-dried to yield 18 g. of light tan material melting at 130°. Recrystallization from toluene yielded 15 g. (0.095 mole, 45%) of colorless flakes melting at 159-160°. Literature value (24), m.p. 162-163°.

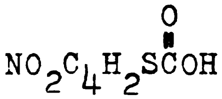
5-Nitro-2-thenal



$NO_2C_4H_2S\overset{\overset{O}{\parallel}}{C}H$

The method of Buu Hoï (25) was used to obtain this material. To a solution of 26 g. (0.232 mole) of 2-thenal dissolved in 50 g. of acetic anhydride contained in a 300-ml. three-necked flask, immersed in an ice bath and fitted with a stirrer, reflux condenser and dropping funnel, was added dropwise a solution containing 19.8 g. of fuming nitric acid (d = 1.49) dissolved in 50 g. of glacial acetic acid, over a period of 15 minutes. The reaction solution was stirred for 90 minutes at 0°. A volume of 200 ml. of water was added, causing the immediate precipitation of a yellow solid. The precipitate was recovered by filtration, washed thoroughly with water, air dried, and recrystallized from 95% ethyl alcohol to yield 32 g. (0.204 mole, 88%) of slightly yellow crystals melting at 71°. Literature value (25), m.p. 77°.

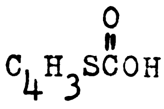
5-Nitro-2-thenoic acid



$NO_2C_4H_2S\overset{\overset{O}{\|}}{C}OH$

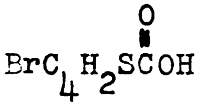
The experimental procedure was adapted from the general method described by Migridichian (26). An 18.8 g. (0.12 mole) quantity of 5-nitro-2-thenal was suspended in a solution prepared from 40.8 g. (0.24 mole) of silver nitrate dissolved in a mixture of 400 ml. of water and 400 ml. of 95% ethyl alcohol contained in a two-liter three-necked flask fitted with a stirrer, reflux condensor, thermometer and dropping funnel. The vigorously stirred reaction mixture was heated to 45° and an alkaline solution containing 19.2 g. (0.48 mole) of sodium hydroxide dissolved in 400 ml. of water was added dropwise at a rate sufficient to maintain the reaction temperature at 45-50°. The addition required 30 minutes, after which the reaction solution was stirred at 50° for another 15 minutes, cooled in an ice bath to room temperature and filtered to remove the metallic silver. After washing the silver with hot water, the combined filtrate and washings were evaporated under an air-jet at room temperature for 48 hours to remove the ethyl alcohol, and reduce the volume of the filtrate to approximately 500 ml. A volume of 500 ml. of ethyl ether was added and the stirred mixture was carefully acidified with concentrated hydrochloric acid. The ether layer was separated. The aqueous layer was extracted with ethyl ether and the combined ether layer and extracts were dried over anhydrous magnesium sulfate. Evaporation of the ether gave 12 g. of a yellow solid melting at 147-150°. Recrystallization from hot water yielded 10 g. (0.058 mole, 48%) of product in the form of light yellow needles melting at 155-157°. Literature value (27), m.p. 158°.

2-Thenoic acid


$C_4H_3S\overset{O}{\overset{\|}{C}}OH$

The method of Hartough and Conley (19) was used to obtain this acid. A solution of sodium hypochlorite was prepared by passing 322 g. (4.50 moles) of chlorine into a tared four-liter beaker containing 440 g. (11.0 moles) of sodium hydroxide dissolved in 600 ml. of water, to which 2500 g. of ice had been added. The chlorine addition was completed in 15 minutes, after which the hypochlorite solution was heated to 60° on a steam-bath. It was transferred quickly to a two-liter three-necked flask fitted with a stirrer, dropping funnel, thermometer and reflux condenser. A 126 g. (1.0 mole) quantity of 2-acetyl thiophene was added dropwise at a rate sufficient to maintain the reaction temperature between 60° and 70°. After the addition of acetyl thiophene was completed, the reaction solution was stirred at 65° for four hours, cooled to room temperature and a solution containing 100 g. of sodium bisulfite dissolved in 200 ml. of water was added. The resulting solution was transferred to two two-liter beakers and acidified with concentrated hydrochloric acid. The white solid product was recovered by filtration, washed with cold water, and recrystallized from water to yield 88 g. (0.69 mole, 69%) of colorless needles melting at 128°. Literature value (19), m.p. 129-130°.

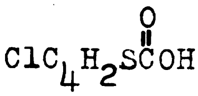
5-Bromo-2-thenoic acid



$BrC_4H_2S\overset{O}{\overset{\|}{C}}OH$

Using the procedure described above, 20.5 g. (0.10 mole) of 5-bromo-2-acetyl thiophene were added in small portions to a solution of sodium hypochlorite prepared from 44 g. (1.10 moles) of sodium hydroxoide, 32.2 g. (0.45 mole) of chlorine and 250 g. of ice. The initial reaction temperature was 60° and was maintained at 60-65° during the addition of the bromoacetyl thiophene by means of an ice-bath. The reaction solution was allowed to come to room temperature, 10 g. of sodium bisulfite dissolved in 20 ml. of water were added and the resulting solution was transferred to a one-liter beaker. After acidification with concentrated hydrochloric acid the colorless precipitate was recovered by filtration and washed with cold water. The dried product was recrystallized from cyclohexane to yield 13 g. (0.062 mole, 62%) of product in the form of white needles melting at 140-141°. Literature value (19), m.p. 141-141.5°.

5-Chloro-2-thenoic acid

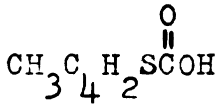


$ClC_4H_2S\overset{O}{\overset{\|}{C}}OH$

Using the procedure described for the preparation of

2-thenoic acid, 32.0 g. (0.20 mole) of 5-chloro-2-acetyl thiophene were added in small portions to a solution of sodium hypochlorite prepared from 88 g. (2.20 moles) of sodium hydroxide, 64.4 g. (0.90 mole) of chlorine and 500 g. of ice. The initial reaction temperature was 60°, and was maintained at 65-70° during the addition of the chloroacetyl thiophene by means of an ice bath. The reaction solution was heated at 65° for an additional one and one-half hours, cooled to room temperature and a solution containing 20 g. of sodium bisulfite dissolved in 40 ml. of water was added. The resulting solution was transferred to a two-liter beaker and acidified with concentrated hydrochloric acid. The colorless precipitate was recovered by filtration, and washed with cold water. The dried product was recrystallized from ligroin (b.p. 90-120°) to yield 23 g. (0.14 mole, 71%) of colorless needles melting at 149-150°. Literature value (19) m.p. 152-153.5°.

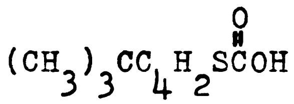
5-Methyl-2-thenoic acid.



$CH_3C_4H_2S\overset{\overset{O}{\|}}{C}OH$

Using the procedure described for the preparation of 2-thenoic acid, 40 g. (0.30 mole) of 5-methyl-2-acetyl thiophene were added dropwise to a solution of sodium hypochlorite prepared from 132 g. (3.30 moles) of sodium hydroxide, 94.5 g. (1.35 moles) of chlorine and 800 g. of ice. The initial reaction temperature was 55°, and was maintained at 75° during the addition of the methylacetyl thiophene by means of an ice bath. After allowing the reaction solution to come to room temperature, 35 g. of sodium bisulfite dissolved in 100 ml. of water were added and the resulting solution was transferred to a four-liter beaker. Acidification with concentrated hydrochloric acid gave a white precipitate which was recovered by filtration and washed with cold water. The dried product was recrystallized from ligroin (b.p. 90-120°) to yield 30 g. (0.20 mole, 70%) of colorless needles, melting at 138°. Literature value (19), m.p. 137-138°.

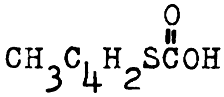
5-*t*-Butyl-2-thenoic acid



$(CH_3)_3CC_4H_2S\overset{\overset{O}{\|}}{C}OH$

Using the procedure described for the preparation of 2-thenoic acid, 54.6 g. (0.30 mole) of 5-*t*-butyl-2-acetyl thiophene were added dropwise to a solution of sodium hypochlorite prepared from 132 g. (3.30 moles) of sodium hydroxide, 96 g. (1.35 moles) of chlorine and 800 g. of ice. The initial reaction temperature was 55°, and rose near the end of the addition of the *t*-butylacetyl thiophene. Therefore, it was necessary to cool the reaction mixture in an ice bath, to maintain its temperature at 70-75°. The reaction solution was heated at 75° for two hours, cooled to room temperature and a solution containing 30 g. of sodium bisulfite dissolved in 100 ml. of water was added. The basic reaction mixture was extracted with ethyl ether to remove neutral material. The aqueous layer was transferred to a two-liter flask fitted with a stirrer and 500 ml. of ethyl ether were added. The stirred reaction mixture was carefully acidified with concentrated hydrochloric acid. The ether layer was separated, the aqueous layer was extracted with ethyl ether and the combined ether layer and extracts were dried over anhydrous magnesium sulfate. Evaporation of the ether on a steam bath yielded 52 g. of a colorless solid. Recrystallization of the crude product from petroleum ether (b.p. 60-90°) gave 40 g. (0.217 mole, 72%) of colorless rosettes melting at 124-125°. Literature value (19), m.p. 128-128.5°.

4-Methyl-2-thenoic acid

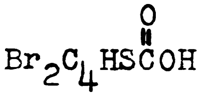


$CH_3C_4H_2S\overset{O}{\overset{\|}{C}}OH$

The method of Schick and Hartough (28) was used to prepare this acid. The reaction was carried out in an atmosphere of dry nitrogen. A 23 g. (1.0 g.at.) quantity of sodium, 15 g. (0.073 g.at.) of mercury and 750 ml. of dry toluene were placed in a two-liter three-necked flask fitted with a stirrer, reflux condenser and thermometer. The mixture was rapidly heated to 95°, then slowly until the sodium amalgamated at 100°. The amalgam mixture was stirred vigorously until the temperature dropped to 35°. The toluene was removed by filtration through a glass wool plug placed in a neck of the flask and the sodium amalgam was immediately covered with 600 ml. of dry ethyl ether. A 98 g. (1.0 mole) quantity of 3-methyl thiophene was added, followed by the dropwise addition of 68.5 g. (0.50 mole) of n-butyl bromide. Cooling of the reaction mixture in an ice bath was necessary to permit a reasonable rate of addition of the n-butyl bromide. Following the addition of the alkyl

bromide, the reaction solution was refluxed for two hours, and then poured onto a slurry of 300 g. of freshly crushed dry ice and 300 ml. of dry ethyl ether. A volume of 100 ml. of absolute alcohol was added to the stirred carbonated mixture, followed by the addition of 350 ml. of water, and the resulting solution was set aside overnight. An additional 200 ml. of water was added to dissolve the gray suspended solid. The aqueous layer was separated and acidified with concentrated hydrochloric acid. The resulting yellow colored precipitate was recovered by filtration, washed with cold water and air-dried to yield 9 g. (0.063 mole, 6%) of a crude product melting at 110-116°. Literature value (28), m.p. 119-121°. Distillation of the ether layer yielded 79 g. (0.81 mole) of unreacted 3-methyl thiophene boiling at 111-113° (1 atm.). Literature value (29), b.p. 115.4° (1 atm.).

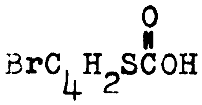
4,5-Dibromo-2-thenoic acid



$Br_2C_4HS\overset{\overset{O}{\|}}{C}OH$

The method of Steinkopf, Jacob and Penz (30) was used to obtain this material. A 450 g. (2.8 moles) quantity of bromine was placed in a one-liter three-necked flask, immersed in an ice bath, and fitted with a stirrer and reflux condenser. To the rapidly stirred bromine, 57 g. (0.445 mole) of 2-thenoic acid were added, in small portions, from a 125 ml. Erlenmeyer flask attached to a neck of the reaction flask by means of a rubber tube. After the addition of the acid was completed, the ice bath was removed and the reaction mixture was stirred at room temperature for one hour. Excess bromine was removed by evaporation at reduced pressure with a water aspirator. The white residue was stirred with 100 ml. of 10% ammonium carbonate solution to remove the last traces of bromine, and was acidified with concentrated hydrochloric acid. The white solid was recovered by filtration and washed with cold water. The dried product was recrystallized from absolute ethyl alcohol to yield 95 g. (0.332 mole, 75%) of colorless solid melting at 224-226°. Literature value (30), m.p. 225-227°.

4-Bromo-2-thenoic acid



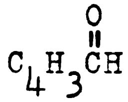
$BrC_4H_2S\overset{O}{\overset{\|}{C}}OH$

The method of S. Gronowitz (31) was used to synthesize this acid. A solution of butyl lithium in ethyl ether was prepared as follows (32). A 120 ml. volume of dry ethyl ether was placed in a 500-ml. three-necked flask fitted with a stirrer, alcohol thermometer, dropping funnel and nitrogen inlet tube. Under a stream of nitrogen, 33 g. (0.475 g.at.) of lithium, cut into chunks of approximately 1 cm.^{3} were added to the ether. An initial quantity of 5.0 g. (0.036 mole) of freshly distilled n-butyl bromide was added to the lithium suspension and the resulting reaction mixture was cooled to -10° in a solid carbon dioxide-isopropyl alcohol bath. An additional 23 g. (0.168 mole) of n-butyl bromide was added to the above described mixture, with vigorous stirring, while maintaining the reaction temperature at ±10-2°. The cooling bath was removed. The reaction mixture was allowed to warm to 10° and was quickly filtered through a glass wool plug directly into a separatory funnel. The latter was fitted to a one-liter three-necked flask, which had been previously charged with a solution containing 800 ml. of dry ethyl ether and 23 g. (0.080 mole) of 3,4-dibromo-2-thenoic acid and cooled to -60° in a solid carbon dioxide-isopropyl alcohol bath. The butyl lithium solution was added to the ether solution of 3,4-dibromo-2-thenoic acid over a period of 15 minutes, while maintaining the temperature of the reaction mixture below -60°. The resulting solution was stirred at -60° for ten minutes after the addition of the butyl lithium solution was completed, and was poured into a beaker containing 600 ml. of water. After being set aside at room temperature overnight, the aqueous layer was separated and the ether layer was extracted with 100 ml. of water. The combined aqueous layer and extracts were acidified with concentrated hydrochloric acid, resulting in the separation from solution of a brown colored oil, which solidified on cooling in an ice bath. The crude product was recovered by filtration, washed with cold water and air-dried at 25° for 24 hours. The yield of crude tan colored 4-bromo-2-thenoic acid was 10.1 g. (0.049 mole, 61%) melting at 100-104°. Literature value (31), m.p. 122-123°.

3-Thenyl bromide $C_4H_3CH_2Br$

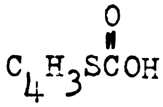
The method of E. Campaigne and B. F. Tullar (33) was followed in the synthesis of this compound, with the exception that α,α'-azodiisobutyronitrile was used as the free-radical source in place of benzoyl peroxide. A solution prepared from 140 ml. of benzene, 44 g. (0.448 mole) of 3-methylthiophene and 1.0 g. (0.00612 mole) of α,α'-azodiisobutyronitrile was refluxed for 15 minutes in a 500 ml., three-necked flask, fitted with a stirrer, Allihn reflux condenser, and a wide-bore reflux condenser having an 18 mm. I.D. inner tube. An intimately mixed powder, consisting of 71 g. (0.40 mole) of N-bromosuccinimide and 1.0 g. (0.00612 mole) of α,α'-azodiisobutyronitrile was added in portions through the top of the wide-bore condenser, over a period of 10 minutes. The reaction flask was cooled to 25° in an ice bath, and the succinimide which had precipitated during the reaction was removed by filtration. The succinimide was washed with 50 ml. of benzene and the combined filtrate and washing was transferred to a 500 ml. flask, equipped with an 8" Vigreux column fitted with a distillation head. A few chips of calcium carbonate were added and the benzene was removed by distillation under reduced pressure (103 mm.). Vacuum distillation of the residue yielded 52 g. of clear liquid boiling at 45-52° (1 mm.), n_D^{25} 1.597. A second fraction of slightly yellow colored liquid boiling at 58-82° (1 mm.), n_D^{25} 1.603 raised the total of product yield to 62 g. (0.350 mole, 78%). Literature values (33), b.p. 76° (1 mm.), n_D^{25} 1.6030. In order to avoid its decomposition, the 3-thenyl bromide was used immediately after it was prepared, for the synthesis of 3-thenal.

3-Thenal



$C_4H_3\overset{\overset{O}{\|}}{C}H$

The method of E. Campaigne, R. C. Bourgeois and W. C. McCarthy (34) was used to synthesize this aldehyde. A total of 62 g. (0.350 mole) of 3-thenyl bromide was added to a solution prepared from 56 g. (0.400 mole) of hexamethylene tetramine and 250 ml. of chloroform contained in a 500 ml., three-necked flask, fitted with a stirrer, reflux condenser and dropping funnel. The addition was carried out at a rate sufficiently rapid to keep the reaction mixture at its reflux temperature. The reaction solution was then heated on a steam bath for 30 minutes and allowed to cool to room temperature, whereupon a white material precipitated from solution. The reaction mixture and precipitate were poured into 200 ml. of water and stirred until the precipitate dissolved. The chloroform layer was separated and washed with water. The combined water layer and extracts were steam distilled until the distillate was no longer cloudy in appearance. The distillate was acidified with concentrated hydrochloric acid and extracted several times with ethyl ether. The ether extracts were dried over anhydrous magnesium sulfate and the ether was removed by distillation on a steam bath. Vacuum distillation of the residue yielded 25 g. (0.223 mole, 64%) of colorless liquid boiling at 75° (12 mm.). Literature value (34), b.p. 72-78° (12 mm.).

3-Thenoic acid 

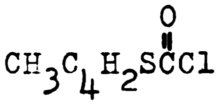
$C_4H_3S\overset{\overset{O}{\|}}{C}OH$

The method of E. Campaigne and W. M. LeSuer (35) was used to synthesize this acid. A suspension of silver oxide was prepared by the addition, with vigorous stirring, of a solution containing 75 g. (0.442 mole) of silver nitrate dissolved in 150 ml. of water to a solution prepared from 35 g. (0.875 mole) of sodium hydroxide and 150 ml. of water and contained in a 500 ml., three-necked flask, fitted with a stirrer and dropping funnel. The reaction mixture was cooled to 0° in an ice bath, and 24 g. (0.207 mole) of 3-thenal were added over a period of ten minutes. Stirring of the reaction mixture at 0° was continued for ten minutes after the addition of the aldehyde was completed. The metallic silver was removed by filtration and was washed with hot water. Acidification of the combined filtrate and washings with concentrated hydrochloric acid precipitated a colorless solid product which was recovered by filtration and was washed with cold water. The crude product was recrystallized from water to yield 21 g. (0.164 mole, 79%) of colorless 3-thenoic acid in the form of needles melting at 137-138°. Literature value (35), m.p. 137-138°.

Preparation of the Thenoyl Chlorides

All of the thenoyl chlorides used in this study were prepared from the corresponding acids by reaction with thionyl chloride. A typical procedure is described below.

5-Methyl-2-thenoyl chloride



$CH_3C_4H_2S\overset{\overset{O}{\|}}{C}Cl$

In a 100 ml. round-bottomed flask fitted with a reflux condenser were placed 10 g. (0.0705 mole) of 5-methyl-2-thenoic acid and 33 g. (0.277 mole) of thionyl chloride. The reaction solution was refluxed on the steam bath for ten hours. Excess thionyl chloride was removed by distillation and the residue was distilled in a micro-distillation apparatus through a 4" Vigreux column to yield 10.1 g. (0.0632 mole, 90%) of a colorless liquid boiling at 99-100° (8 mm.). Literature value, (36) b.p. 102° (16 mm.).

The thenoyl chlorides prepared in this investigation, together with their boiling points, literature references and yields are summarized in Table 1. Three of these thenoyl chlorides have not been previously reported. The amide of 5-methoxy-2-thenoyl chloride was prepared by passing gaseous ammonia into an ethereal solution of the acid chloride. An elementary analysis was run on the amide, since the expected bis(5-methoxy-2-thenoyl) peroxide could not be prepared from the acid chloride.

Preparation of the Bis(2-Thenoyl) Peroxides

The bis(2-thenoyl) peroxides used in this study, with the exception of 5-methyl-bis(2-thenoyl) peroxide, were prepared by reaction of the corresponding acid chloride with aqueous sodium peroxide. The acid chloride was dissolved in an inert organic solvent, which coated the crystalline peroxide as it

TABLE I

PREPARATION OF THE THENOYL CHLORIDES

Thenoyl Chloride	Yield %	B.P. °C.	Literature Reference
2-Thenoyl chloride	93	92 (18 mm.)	15
5-Bromo-2-thenoyl chloride	92	80 (2 mm.)	36
5-Chloro-2-thenoyl chloride	80	103 (15 mm.)	36
5-Methyl-2-thenoyl chloride	89	99-100 (8 mm.)	36
5-_t_-Butyl-2-thenoyl chloride	82	110 (4 mm.)	44
5-Methoxy-2-thenoyl chloride	71	120 (5 mm.)	not reported*
5-Nitro-2-thenoyl chloride	90	105-110 (2 mm.)	27
4-Methyl-2-thenoyl chloride	64	68-68.5 (2 mm.)	not reported
4-Bromo-2-thenoyl chloride	84	75-83 (1 mm.)	not reported
3-Thenoyl chloride	88	100 (30 mm.)	37

*Elementary analysis of 5-methoxy-2-thiophene carboxamide

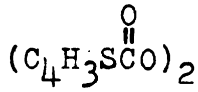
Calc'd for $C_6H_7NO_2S$: C, 45.84; H, 4.49; N, 8.97; S, 20.40

Found: C, 45.73; H, 4.33; N, 8.73; S, 20.35

formed, and thus protected it from reaction with the basic aqueous sodium peroxide. The peroxides are colorless, crystalline solids at room temperature, with the exception of bis(5-nitro-2-thenoyl) peroxide which is a light yellow colored, crystalline solid. The peroxides were stored in a vacuum dessicator which was placed in a refrigerator. The stability of the peroxides over a period of time under these conditions is indicated by the fact that bis(2-thenoyl) peroxide was found to be 99.2% pure, by iodometric titration, after ten months of storage.

The bis(2-thenoyl) peroxides prepared in this investigation, together with the solvents for recrystallization, yields, melting points and purity by iodometric titration are summarized in Table 2.

Bis(2-thenoyl) peroxide



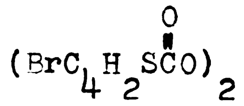
$(C_4H_3S\overset{O}{\overset{\|}{C}}O)_2$

A volume of 50 ml. of water, contained in a 500-ml. three-necked flask fitted with a stirrer, thermometer and dropping funnel was cooled to 0° in an ice bath. With stirring, 5 g. (0.064 mole) of sodium peroxide were added in small portions. A solution prepared from 14.6 g. (0.10 mole) of 2-thenoyl chloride and 30 ml. of dry toluene was added dropwise at 0°, to the aqueous peroxide solution, with vigorous stirring, over a period of 30 minutes. A colorless insoluble material began to form as soon as the addition of acid chloride was begun. The reaction mixture was stirred at 0° for two hours following the addition of the acid chloride. The colorless, crystalline product was recovered by filtration and was washed with ice water. After drying at 0°, in a vacuum dessicator for 48 hours, the crude product was recrystallized from the minimum amount of chloroform by the addition of cyclohexane. The yield of dense, colorless crystals was 5.1 g. (0.020 mole, 40%), melting at 100-101°. Literature value (15), m.p. 103°. The product decomposed and became red in color at the m.p., but did not detonate. Analysis of the product for carbon, hydrogen and sulfur gave the following results:

Calc'd. for $C_{10}H_6O_4S_2$: C, 47.23; H, 2.38; S, 25.22

Found: C, 47.52; H, 2.40; S, 25.43

Bis(5-bromo-2-thenoyl) peroxide



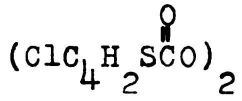
$(BrC_4H_2S\overset{\overset{O}{\|}}{C}O)_2$

Using the apparatus and general procedure described above, 1.95 g. (0.025 mole) of sodium peroxide were added at 0°, in small portions, to 25 ml. of water. A solution containing 10.0 g. (0.044 mole) of 5-bromo-2-thenoyl chloride and 35 ml. of dry cyclohexane was added all at once, at 0°, to the vigorously stirred aqueous peroxide solution. A colorless solid began to form immediately. The reaction mixture was stirred at 0°, for one and one-half hours. The colorless, crystalline product was recovered by filtration and was washed with ice water. After drying at 0°, for 48 hours in a vacuum dessicator, the crude product was recrystallized from the minimum amount of n-butyl ether (preheated to 50°) by the addition of chloroform. The yield of colorless peroxide was 4.0 g. (0.0097 mole, 44%) melting at 130°. Upon melting, the material became red in color, and detonated after being heated at its melting point for two minutes. Analysis of the product for carbon, hydrogen, sulfur and bromine gave the following results:

Calc'd. for $C_{10}H_4Br_2O_4S_2$: C, 29.14; H, 0.978;
S, 15.56: Br, 38.79

Found: C, 28.98; H, 1.10; S, 15.56; Br, 38.65

Bis(5-chloro-2-thenoyl) peroxide



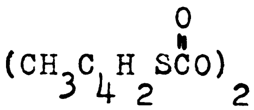
$(ClC_4H_2S\overset{\overset{O}{\|}}{C}O)_2$

Using the apparatus and general procedure described for the preparation of bis(2-thenoyl) peroxide, 2.50 g. (0.032 mole) of sodium peroxide were added at 0°, in small portions, to 35 ml. of water. A solution containing 10.0 g. (0.056 mole) of 5-chloro-2-thenoyl chloride and 35 ml. of dry cyclohexane was added all at once, at 0°, to the vigorously stirred aqueous peroxide solution. A colorless solid began to form immediately. The reaction mixture was stirred at 0° for one and one-half hours. The colorless, crystalline product was recovered by filtration and was washed, with ice water. It was then washed with four 25 ml. portions of cold petroleum ether (b.p. 30-60°) to remove unreacted 5-chloro-2-thenoyl chloride. After drying at 0°, for 48 hours in a vacuum dessicator, the crude product was recrystallized from petroleum ether (b.p. 30-60°). The yield of faintly yellow colored feathery clusters was 4.4 g. 0.0271 mole, 48%) melting at 110°. Upon melting, the material became red in color, but did not detonate. Analysis of the product for carbon, hydrogen, sulfur and chlorine gave the following results:

Calc'd. for $C_{10}H_4Br_2O_4S_2$: C, 37.16; H, 1.25; S, 19.84; Cl, 21.94

Found: C, 37.48; H, 1.66; S, 19.84; Cl, 21.86

Bis(5-methyl-2-thenoyl) peroxide



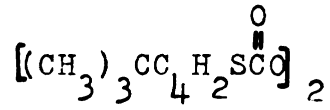
$(CH_3C_4H_2S\overset{O}{\overset{\|}{C}}O)_2$

Using the apparatus and general procedure described for the preparation of bis(2-thenoyl) peroxide, 3.1 g. (0.040 mole) of sodium peroxide were added at 0°, in small portions, to 30 ml. of water. A solution containing 10 g. (0.062 mole) of 5-methyl-2-thenoyl chloride and 30 ml. of dry toluene was added dropwise, at 0°, over a period of 15 minutes to the vigorously stirred aqueous peroxide solution. The reaction solution was stirred at 0°, for an additional two and one-half hours. About 15 minutes after the reaction was begun, a colorless insoluble material began to separate from solution. The colorless, crystalline product was recovered by filtration and was washed with ice water. After drying at 0°, for 48 hours in a vacuum dessicator, the crude product was recrystallized from the minimum amount of benzene by the addition of petroleum ether (b.p. 30-60°). The yield of colorless peroxide was 3.1 g.

(0.0110 mole, 35%) melting at 104°. Upon melting, the material became red in color and detonated. Analysis of the product for carbon, hydrogen and sulfur gave the following results:

Calc'd. for $C_{12}H_{10}O_4S_2$: C, 51.05; H, 3.57; S, 22.72
Found: C, 51.12; H, 3.62; S, 22.58

Bis(5-*t*-butyl-2-thenoyl) peroxide



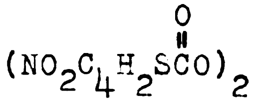
$$\left[(CH_3)_3CC_4H_2S\overset{O}{\overset{\|}{C}}O\right]_2$$

Using the apparatus and general procedure described for the preparation of bis(2-thenoyl) peroxide, 1.92 g. (0.0248 mole) of sodium peroxide were added at 0°, in small portions, to 25 ml. of water. A solution containing 7.0 g. (0.045 mole) of 5-*t*-butyl-2-thenoyl chloride and 20 ml. of dry cyclohexane was added all at once, at 0°, to the vigorously stirred aqueous peroxide solution. The reaction solution was stirred, at 0°, for two and one-half hours. About 45 minutes after the reaction was begun, a colorless insoluble material began to separate from solution. The colorless, crystalline product was recovered by filtration and was washed with ice water. After drying at 0°, for 48 hours in a vacuum dessicator, the crude product was recrystallized from petroleum ether (b.p. 30-60°). The yield of colorless peroxide was 2.0 g. (0.00546 mole, 24%), melting at 93°. The material became red in color at 95°, but did not detonate. Analysis of the product for carbon, hydrogen and sulfur gave the following results:

Calc'd. for $C_{18}H_{22}O_4S_2$: C, 58.99; H, 6.05; S, 17.50

Found: C, 59.16; H, 6.00; S, 17.56

Bis(5-nitro-2-thenoyl) peroxide



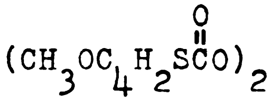
$(NO_2C_4H_2S\overset{O}{\overset{\|}{C}}O)_2$

Using the apparatus and general procedure described for the preparation of bis(2-thenoyl) peroxide, 1.32 g. (0.017 mole) of sodium peroxide were added at 0°, in small portions, to 35 ml. of water. A solution containing 5.0 g. (0.0260 mole) of 5-nitro-2-thenoyl chloride and 14 ml. of dry benzene was added all at once, at 0°, to the vigorously stirred aqueous peroxide solution. A bright yellow colored material began to precipitate immediately. The reaction mixture was stirred at 0°, for two hours and the yellow colored product was separated by filtration. The filtrate was acid to pHydrion paper, indicating the presence of 5-nitro-2-thenoic acid. The yellow colored peroxide was therefore washed with cold dilute sodium hydroxide solution until the washings were basic to pHydrion paper, and it was finally washed with cold water. After drying at 0°, in a vacuum dessicator for 48 hours, the crude product was recrystallized from the minimum amount of chloroform by the addition of petroleum ether (b.p. 30-60°). The yield of light yellow colored product was 1.5 g. (0.00437 mole, 34%) melting at 120-122°. The material darkened and became red in color at 125°, but did not detonate. Analysis of the product for carbon, hydrogen, nitrogen and sulfur gave the following results:

to 35 ml. of water. A solution containing 7.5 g. (0.0513 mole) of 3-thenoyl chloride and 10 ml. of dry toluene was added dropwise over a period of one-half hour to the vigorously stirred aqueous peroxide solution. As soon as the reaction was begun, a colorless insoluble material began to separate from solution. Stirring of the reaction mixture at 0°, was continued for two hours after the addition of acid chloride was completed. The colorless, crystalline product was recovered by filtration and washed with ice water. After drying at 0°, for 48 hours in a vacuum dessicator, the crude product was recrystallized from cyclohexane (preheated to 60°). The yield of colorless needles was 3.4 g. (0.0134 mole, 52%), melting at 120°. Upon melting, the material became red in color, and detonated. Analysis of the product for carbon, hydrogen and sulfur gave the following results:

Calc'd. for $C_{10}H_6O_4S_2$: C, 47.23; H, 2.38; S, 25.22
Found: C, 47.41; H, 2.22; S, 25.19

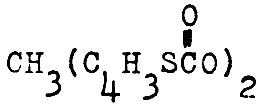
Bis(5-methoxy-2-thenoyl) peroxide



$(CH_3OC_4H_2S\overset{O}{\overset{\|}{C}}O)_2$

Using the apparatus and general procedure described for the preparation of bis(2-thenoyl) peroxide, 1.87 g. (0.0240 mole) of sodium peroxide was added at 0°, in small portions, to 25 ml. of water. A solution containing 7.0 g. (0.039 mole) of 5-methoxy-2-thenoyl chloride and 24 ml. of dry cyclohexane was added in one portion at 0°, to the vigorously stirred aqueous peroxide solution. A yellow colored solid material began to form as soon as the reaction was started. The solid material appeared to darken after about 15 minutes of reaction. Stirring of the reaction mixture was immediately discontinued, and the solid product was separated by vacuum filtration on a pre-cooled sintered-glass Beuchner funnel. At no time during the filtration and subsequent washing with ice water was the crude product allowed to be drawn free of liquid by the vacuum filtration. However, upon attempting to transfer the wet crude product from the funnel to a container, it suddenly began to decompose with the evolution of fumes and the formation of a dark brown colored tarry mass. The tarry residue gave a negative peroxide test when it was dissolved in glacial acetic acid and treated with aqueous sodium iodide. In view of the apparent instability of the compound, further attempts at its preparation were considered impractical, and the synthesis of the compound was, therefore, not pursued.

5-Methyl bis(2-thenoyl) peroxide



$CH_3(C_4H_3S\overset{\overset{O}{\|}}{C}O)_2$

The procedure of Braun (38) was adapted to the preparation of the sodium perthenoate used in this synthesis. A solution prepared from 5.2 g. (0.0224 g.at.) of sodium in 20 ml. of absolute methanol (C.P., distilled from barium oxide) contained in a 200 ml. Erlenmeyer flask was cooled to -5° in an ice-salt bath. A solution containing 5.1 g. (0.0202 mole) of bis (2-thenoyl) peroxide in 20 ml. of chloroform was cooled to 0°, and slowly added to the vigorously shaken sodium methoxide solution maintained at 0°. Following the addition of the peroxide, the reaction solution was shaken for another ten minutes at 0°, transferred to a separatory funnel and extracted with one 50 ml. portion of water containing some crushed ice. The aqueous layer was separated and extracted with two 10 ml. portions of cold chloroform to remove the methyl thenoate. The aqueous layer, containing the sodium perthenoate, was transferred to a 500-ml., three-necked flask fitted with a stirrer, condenser and dropping funnel and cooled to 0° by means of an ice bath. A solution containing 2.4 g. (0.015 mole) of 5-methyl-2-thenoyl chloride and 50 ml. of dry cyclohexane was added dropwise during a period of 15 minutes. The reaction solution was stirred an additional one hour, but no solid material separated from solution during that time. Therefore, 100 ml. of ethyl ether was added to the reaction solution, and the organic layer was separated. The aqueous layer was extracted with two 50 ml. portions of ethyl ether and the organic layer and ether extracts were combined and dried over anhydrous magnesium sulfate. Evaporation of the ether on a steam bath yielded a colorless solid. Recrystallization of the crude product was accomplished by dissolving the material in the minimum amount of chloroform, adding petroleum ether (b.p. 30-60°) and concentrating the solution, at room temperature, under reduced pressure. The yield of colorless product was 0.90 g. (0.00336 mole, 22% based on 5-methyl-2-thenoyl chloride), melting at 78-80°. Upon melting, the material remained clear, and did not detonate or decompose. It took on a red coloration upon heating to 100°, but did not detonate. Analysis of the product for carbon, hydrogen and sulfur gave the following results:

Calc'd. for $C_{11}H_7O_4S_2$: C, 49.24; H, 3.01; S, 23.90
Found: C, 49.31; H, 3.21; S, 23.70

Preparation of 3,4-Dichlorostyrene

1(3,4-Dichlorophenyl) ethanol

The method of Lock and Bock (39) was used to prepare this intermediate alcohol. A 20 g. (0.823 g.at.) quantity of dry magnesium turnings was placed in a two-liter three-necked flask fitted with a stirrer, Allihn condenser and separatory funnel. The funnel was charged with a solution containing 96 g. (0.677 mole) of methyl iodide dissolved in 800 ml. of dry ethyl ether. A few milliliters of the methyl iodide solution were added to the magnesium turnings to initiate the reaction, after which the addition was continued at a rate sufficient to cause the ether to reflux gently. After the addition of the iodide was completed, a solution containing 104 g. (0.597 mole) of 3,4-dichlorobenzaldehyde dissolved in 400 ml. of dry ether was added to the Grignard mixture at a rate sufficient to cause the solvent to reflux gently. After the aldehyde had been added, the reaction mixture was refluxed on a steam bath for 15 minutes. It was cooled to room temperature, and poured over 200 g. of ice cubes. A solution prepared from 60 g.

TABLE 2

PREPARATION OF THE BIS(2-THENOYL) PEROXIDES

Peroxide	Solvent for Recrystallization	Yield %	M.P. °C.	Purity %
Bis(2-thenoyl)	Chloroform-cyclohexane	40	100-101	98.9
Bis(5-bromo-2-thenoyl)	*n*-Butyl ether-chloroform	44	130	99.5
Bis(5-chloro-2-thenoyl)	Pet. ether (b.p. 30-60°)	48	110	100
Bis(5-methyl-2-thenoyl)	Pet. ether (b.p. 30-60°)	35	104	99.2
Bis(5-*t*-butyl-2-thenoyl)	Pet. ether (b.p. 30-60°)	24	93	99.2
Bis(5-nitro-2-thenoyl)	Chloroform-pet. ether (b.p. 30-60°)	34	120-122	98.9
Bis(4-methyl-2-thenoyl)	Benzene-pet. ether (b.p. 30-60°)	54	113	99.6
Bis(4-bromo-2-thenoyl)	Pet. ether (b.p. 30-60°)	23	126	100
Bis(3-thenoyl)*	Cyclohexane	52	120	100
5-Methyl bis(2-thenoyl)	Chloroform-pet. ether (b.p. 30-60°)	22	78-80	98.0

*Although it is not structurally a bis(2-thenoyl) peroxide, this peroxide was prepared and studied for purposes of comparison.

(1.13 moles) of ammonium chloride and 300 ml. of water was added to the hydrolyzed reaction mixture to dissolve the magnesium salts, and this was followed by the addition of 50 ml. of concentrated hydrochloric acid. The ether layer was separated and extracted with two 200 ml. portions of 0.1 N sodium thiosulfate solution. After washing with water, the ether layer was separated and dried over anhydrous magnesium sulfate. The ether was removed by distillation on a steam bath and the residue was vacuum distilled through an 8" Vigreux column to yield 92 g. (0.485 mole, 81%) of colorless liquid boiling at 125-129° (3 mm.). Literature value (40), b.p. 125-130 (3-4 mm.).

1(3,4-Dichlorophenyl) ethyl acetate

The method described by Elderfield, Gensler, Brody, Head, Dickerman, Wiederhold, Kremer, Hageman, Kreysa, Griffing, Kupchan, Newman and Maynard (41), was modified for the preparation of this ester. A solution prepared from 92 g. (0.485 mole) of 1(3,4-dichlorophenyl) ethanol and 70 g. (0.686 mole) of acetic anhydride was contained in a 500-ml. two-necked flask fitted with a stirrer and reflux condenser. The stirred reaction solution was gently refluxed for two hours and was allowed to cool to 25°. A 200 ml. volume of water was added to the reaction solution and it was stirred for an additional 45 minutes. The organic layer was separated and washed with 10% sodium carbonate solution until the washings were neutral to pHydrion paper. After washing with water, the organic layer was dried over anhydrous magnesium sulfate. Vacuum distillation yielded 80 g. (0.345 mole, 71%) of a clear liquid boiling at 120-123° (2 mm). Literature value (40), b.p. 100-102° (4 mm.).

3,4-Dichlorostyrene

The method of Swain, Stockmayer and Clarke (4), was used to prepare this compound. A 12" electrically-heated pyrex column having an I.D. of 18 mm., was filled to a height of 8" with 1 cm. lengths of pyrex rod. Under a steam of purified nitrogen, 80 g. (0.345 mole) of 1(3,4-dichlorophenyl) ethyl acetate was dropped on the vertically supported column, at a rate of one drop per second, while maintaining the temperature of the column at 550° by means of a chromel-alumel thermocouple in conjunction with a Leeds-Northrup galvanometer. The dark brown colored pyrolysis product was washed with three 50 ml. portions of 10% sodium carbonate solution. After washing with water, the crude product was dried over anhydrous magnesium sulfate. Vacuum distillation yielded 40 g. (0.232 mole, 67%) of a clear liquid boiling at 74-75° (2 mm.), n_D^{20} 1.5843. Literature values (40), b.p. 88-89° (5 mm.), n_D^{20} 1.5844.

Product Analyses

Products of the Decomposition of Bis(2-thenoyl) peroxide in Carbon Tetrachloride in the Absence of 3,4-Dichlorostyrene

The apparatus consisted of a standard-taper two-liter three-necked flask, fitted with a Graham condenser to the top of which was attached a train for collecting exit gases. The reaction flask was also equipped with a water cooled plug, and a nitrogen inlet tube extending to the bottom of the flask. The exit gases were led, in turn, through a cold trap immersed in a dry ice-isopropyl alcohol bath, a tared ascarite U-tube containing ascarite and anhydrone in a volume ratio of two to one, a protective ascarite U-tube and a protective anhydrone U-tube. A special carbon tetrachloride insoluble stop-cock grease (42) was used on the standard-taper joints to prevent contamination of the peroxide solution.

An 800 ml. volume of purified carbon tetrachloride (page 9) was placed in the flask and flushed with purified nitrogen, at 25°, for one half hour. A 10.237 g. (0.0403 mole) quantity of bis(2-thenoyl peroxide was added to the carbon tetrachloride and the reaction solution was heated under a steady stream of purified nitrogen, at 75 ±0.2° for 44 hours. At this point, the solution had taken on a brownish coloration and a dark brown colored material had precipitated from solution. The product isolation procedure was similar to that described by Ford and Mackay (15). The gain in weight of the ascarite U-tube after the decomposition showed that 0.713 g. of carbon dioxide had been evolved. The carbon tetrachloride was removed from the reaction mixture by low pressure distillation through a 12" glass helix packed column. The dark colored residue was extracted with five 100 ml. portions of hot ethyl ether, which left 4.7 g. of a brown powdery residue. This residue was dissolved in hot chloroform and treated with norite. The addition of methanol to the chilled chloroform filtrate gave a brown colored amorphous powder which melted with decomposition, at 155-167°. Analysis of this material for carbon, hydrogen and sulfur gave the following results:

Found: C, 47.42; H, 2.65; S, 27.64

The combined ether extracts were washed with five 50 ml. portions of 2 N potassium carbonate solution to separate any 2-thenoic acid, and then with water, followed by drying over anhydrous magnesium sulfate. The ether was removed by distillation, through a 12" Vigreux column, on a steam bath. The viscous dark brown colored residue was distilled in a molecular still at a pressure less than 2×10^{-3} mm. The small amount of yellow distillate collected could not be identified.

The potassium carbonate extracts and water washings were combined and acidified with concentrated hydrochloric acid. The acidified solution was extracted with five 50 ml. portions of ethyl ether. Evaporation of the ether with an air-stream yielded 2.1 g. of 2-thenoic acid melting at 124-126°.

Carbon Dioxide Analyses

The carbon dioxide determinations were carried out in a standard-taper, single-necked 250-ml. flask modified with a sealed-on nitrogen inlet tube extending almost to the bottom of the flask and a sealed-on Graham condenser. A standard-taper cold finger fitted into the neck. The exit gases passed through a sealed-on stopcock at the top of the condenser, and then successively, through a cold trap maintained at dry ice-isopropyl alcohol temperature, a tared ascarite U-tube containing ascarite and anhydrone in a volume ratio of two to one, a protective ascarite U-tube and a protective anhydrone U-tube.

The following experimental procedure was used in a typical carbon dioxide determination. A 50 ml. volume of purified carbon tetrachloride (page 9) was placed in the flask. The latter was immersed in an oil bath thermostated at 75±0.2° and a slow stream of purified nitrogen was passed through the system for a period of 24 hours. The ascarite U-tube was removed and weighed. A 0.328 g. (0.00129 mole) quantity of bis(2-thenoyl) peroxide and 1.4 ml. (0.010 mole) of 3,4-dichlorostyrene were dissolved in the nitrogen flushed carbon tetrachloride. The ascarite U-tube was placed in the system and the nitrogen flow was resumed. After 72 hours the ascarite U-tube was removed and found to have gained .005 g. in weight, corresponding to 0.000114 mole of carbon dioxide.

The results of the carbon dioxide determinations are summarized in Table 3.

TABLE 3

CARBON DIOXIDE ANALYSES

Peroxide	Peroxide (g.)	3,4-Dichloro-styrene (ml.)	CO_2 (g.)	CO_2 (mole %)
Bis(2-thenoyl)	0.198	0	0.016	23.4
Bis(2-thenoyl)	0.328	1.4	0.005	4.4
Bis(3-thenoyl)	0.190	0	0.036	54.7
Bis(3-thenoyl)	0.252	1.4	0.003	3.4

*Calculated on the basis of two moles of carbon dioxide theoretically possible per mole of peroxide decomposed.

Kinetics

The rates of thermal decomposition of the bis(2-thenoyl) peroxides were followed by iodometric titration of samples of the peroxide solutions, which had been heated for definite intervals of time. The decompositions were carried out in an electrically-heated mineral oil bath, the temperature of which could be controlled to ±0.2° by means of a Fisher-Serfass Electronic Relay.

The peroxide solutions were contained in 10 ml. Kimble Neutraglass ampoules. The ampoules were cleaned (4) by immersing them in warm cleaning solution for 15 minutes. They were then rinsed with water, immersed in dilute ammonium hydroxide solution for one hour, thoroughly rinsed with water, given a final rinse with acetone and dried at 100° for 12 hours.

The nitrogen used to remove oxygen from the peroxide solutions was purified (43) by bubbling it successively through, two towers containing 200 ml. of Fieser's solution, a tower containing 200 ml. of saturated lead acetate solution, a tower containing 300 ml. of concentrated sulfuric acid and finally through a tower containing anhydrous calcium chloride.

The approximately 0.01N standard thiosulfate solution was prepared by dissolving 4.4 g. of Analytical Reagent grade sodium thiosulfate in two liters of freshly boiled, distilled water. A quantity of 0.2 g. of sodium carbonate was added as a preservative. The solution was standardized with Analytical Reagent grade potassium iodate, using the titration technique described below for the titration of the peroxide solutions.

The following experimental procedure was used in a typical kinetic determination. A quantity of 0.315 g. (0.00124 mole) of bis(2-thenoyl) peroxide and 1.4 ml. (0.010 mole) of 3,4-dichlorostyrene was made up to volume with purified carbon tetrachloride (page 9) in a 50 ml. volumetric flask. The solution was cooled to 0° in an ice bath and purged of oxygen by bubbling purified nitrogen into the flask for 15 minutes. The solution was warmed to room temperature and six 5-ml. samples were pipetted into ampoules. The ampoules were sealed at room temperature, under a nitrogen atomsphere, with an air-gas torch. They were placed in a metal rack and the rack was immersed in an oil bath, maintained at the desired temperature. A period of three minutes was allowed for the samples to reach the temperature of the bath, thus zero time was assumed to be three minutes after the ampoules were immersed in the bath. At various time intervals an ampoule was removed from the bath and immediately quenched by immersion in cold water. The tip of the ampoule was broken off and the contents were emptied into a 125 ml. Erlenmeyer flask. The ampoule was rinsed thoroughly with carbon tetrachloride and the rinsings were placed in the flask. Several small lumps of dry ice were placed in the flask and 10 ml. of Analytical Reagent grade acetic anhydride and 1 g. of Analytical Reagent grade sodium iodide were added. The solution was stoppered with a cork and was stirred for ten minutes by means of a magnetic stirrer. A volume of 50 ml. of distilled water was added and the rapidly-stirred solution was immediately titrated with standard sodium thiosulfate solution. The dead-stop method (45) was used to determine the end-point in the titration, employing a Fisher Electropode in conjunction with a pair of platinum electrodes immersed in the vigorously-stirred solution. The end-point corresponded to the increment of thiosulfate added, after which current failed to register on the galvanometer of the Electropode. It was found that no blank was necessary as long as dry ice was added. In the absence of dry ice a positive correction of 0.10 ml. was necessary. Duplicate samples were titrated during several kinetic determinations (see Tables 14, 22, 23, 27, 28 and 30) and the average deviation varied from 1 to 15 parts per thousand. As would be expected, the average deviation usually increased in proportion to the percent peroxide decomposed. Plots of the logarithm of the peroxide concentration versus time for bis(2-thenoyl) peroxide determined at three different temperatures are shown in Figure I. Similar plots for the other thenoyl peroxides studied are shown in the Appendix. Several of the kinetic determinations carried out in the preliminary phases of this investigation, in which styrene was used as a free-radical inhibitor, are also shown in the Appendix.

Effects of Variables on the Kinetics

Oxygen

The effect of oxygen on the rate of decomposition of the thenoyl peroxides was demonstrated by allowing one ampoule to remain open to the atmosphere during a given kinetic determination. The volume of standard thiosulfate solution required to titrate the exposed sample was slightly larger than that required for a sealed sample heated for the same period of time (see Tables 25 and 31). These results indicate that the presence of oxygen increases the concentration of material oxidized by iodide ion during the titration.

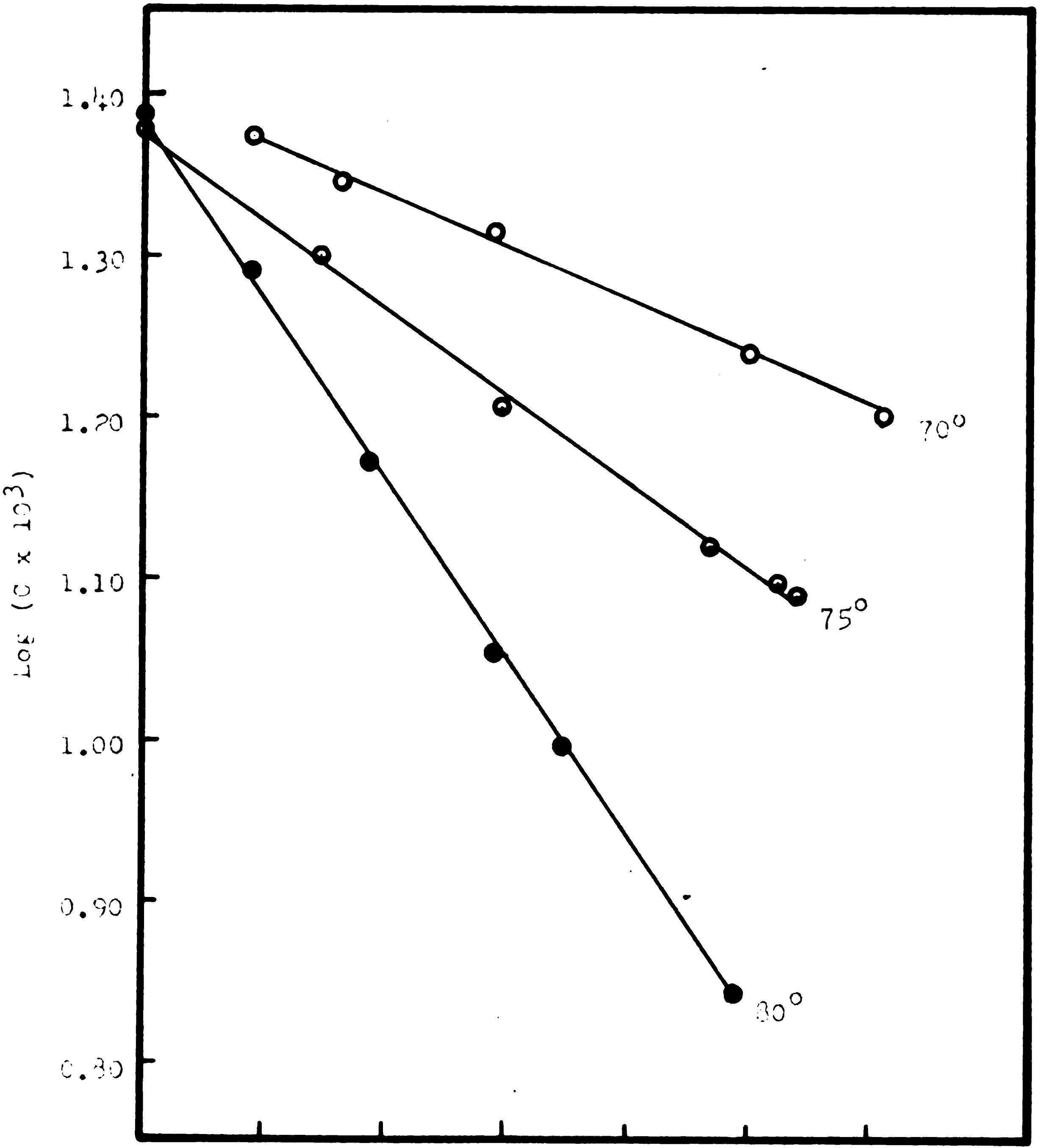


Figure I. Log peroxide concentration versus time for the decomposition of bis(2-thenoyl) peroxide in carbon tetrachloride in the presence of 0.20 M 3,4-dichlorostyrene at 70°, 75° and 80°.

TABLE 4

DECOMPOSITION OF BIS(2-THENOYL) PEROXIDE IN THE PRESENCE OF 0.20 M 3,4-DICHLOROSTYRENE IN CARBON TETRACHLORIDE AT 70°

ml. = milliliters of 0.01109 N sodium thiosulfate

C = molarity of peroxide solution

t = time in minutes

Sample	ml.	$C \times 10^3$	$\log (C \times 10^3)$	t
1	21.27	23.59	1.37273	90
2	20.00	22.18	1.34596	165
3	18.62	20.65	1.31492	290
4	15.68	17.39	1.24030	500
5	14.32	15.89	1.20112	610

$k = 7.54 - \quad \times 10^{-4}$

TABLE 5

DECOMPOSITION OF BIS(2-THENOYL) PEROXIDE IN THE PRESENCE OF 0.20 M 3,4-DICHLOROSTYRENE IN CARBON TETRACHLORIDE AT 75°

ml. = milliliters of 0.01109 N sodium thiosulfate
C = molarity of peroxide solution
t = time in minutes

Sample	ml.	C x 10^3	log (C x 10^3)	t
1	21.68	24.00	1.38021	0
2	17.99	19.95	1.29994	135
3	14.48	16.06	1.20575	295
4	11.89	13.19	1.12024	450
5	11.30	12.53	1.09795	490
6	10.48	11.62	1.06521	540

$k = 1.33 \pm .02 \times 10^{-3}$

TABLE 6

DECOMPOSITION OF BIS(2-THENOYL) PEROXIDE IN THE PRESENCE OF 0.20 M 3,4-DICHLOROSTYRENE IN CARBON TETRACHLORIDE AT 80°

ml. = milliliters of 0.01109 N sodium thiosulfate

C = molarity of peroxide solution

t = time in minutes

Sample	ml.	$C \times 10^3$	$\log (C \times 10^3)$	t
1	22.09	24.49	1.38899	0
2	17.55	19.46	1.28914	90
3	13.43	14.89	1.17289	185
4	10.22	11.33	1.05423	290
5	8.94	9.914	0.99625	370
6	6.29	6.976	0.84361	485

$k = 2.55 \pm .09 \times 10^{-3}$

Surface area of the ampoules

The surface area of one ampoule in a given kinetic determination was greatly increased by the addition of glass wool. The volume of standard thiosulfate solution required to titrate this sample was slightly smaller than that required for a sample not containing glass wool, which had been heated for the same period of time (see Table 31). Since the ampoules were uniform in shape and size, it was felt that a slight variation in the surface area of the ampoules would offer no serious interference with the kinetic determinations.

Light

The ampoules were protected from direct light by covering the constant-temperature bath with aluminum foil during the kinetic determinations.

Initial peroxide concentration

In order to determine the affect of a change in the initial peroxide concentration on the rate of the decomposition of the thenoyl peroxides, several kinetic runs were made in which the initial peroxide concentration was varied by a factor of two (see Figures XI and XII), and all other variables were held constant. With bis(2-thenoyl) peroxide the rate was not affected. With bis(5-methyl-2-thenoyl) peroxide, bis(4-methyl-2-thenoyl) peroxide and bis(5-chloro-2-thenoyl) peroxide, there was a slight decrease in rate on halving the initial concentration. It would be expected that if induced decomposition were occuring, a decrease in the initial peroxide concentration would decrease the overall rate of decomposition. Thus, it appears that very little induced decomposition occurs under the experimental conditions employed in this study.

Nature of the free-radical inhibitor

Styrene was used as the free-radical inhibitor in the preliminary phases of this inventigation, and was found to be effective in eliminating the induced decomposition. Later in these studies, 3,4-dichlorostyrene was tested and found to be equally effective. In the presence of 0.20 M quantities of either monomer (cf. Tables 5 and 31, and 18 and 32), the rates of decomposition of bis(2-thenoyl) peroxide are the same, as is the case of bis(5-t-butyl-2-thenoyl) peroxide. However, the overall rate of decomposition of bis(5-nitro-2-thenoyl) peroxide, in which a large amount of induced decomposition would be expected to occur (4) appears to be somewhat slower in 3,4-dichlorostyrene than in styrene (see Figure XIII). With neither inhibitor was the induced decomposition of the nitroperoxide completely eliminated, as evidenced by the non-linearity of the rate curves shown in Figure XIII.

Breitenbach and Karlinger (14) carried out the decomposition of 0.001 M bis(2-thenoyl) peroxide in carbon tetrachloride in the presence of 0.10 M styrene, and found that the resulting polymer contained 0.39% sulfur. In this investigation it was found that in the decomposition of 0.20 M bis(2-thenoyl) peroxide in carbon tetrachloride in the presence of 0.20 M 3,4-dichlorostyrene (approximate concentrations used in the kinetic determinations), the polymer that resulted after heating at 75° for 60 hours also gave a positive test for sulfur (46). The colorless polymer was precipitated by the addition of methanol to the chilled decomposition mixture.

DISCUSSION

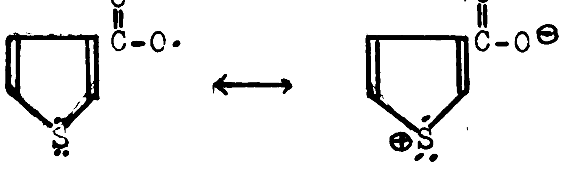
This investigation can be divided into two parts, the preparation of the substituted bis(2-thenoyl) peroxides, and a study of the kinetics of their thermal decomposition.

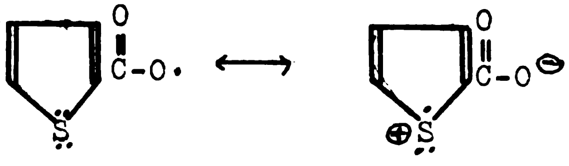
The peroxides investigated, with the exception of 5-methyl bis(2-thenoyl) peroxide, were readily prepared by the interaction of the appropriate thenoyl chloride with aqueous sodium peroxide. In many of the syntheses, toluene was found to be a poor solvent to employ for the purpose of adding the acid chloride to the aqueous sodium peroxide, inasmuch as the reaction product, the bis(thenoyl) peroxide, failed to precipitate from the two phase reaction mixture (13). However, in the cases where this occured, substitution of cyclohexane or benzene for toluene produced the desired solubility effect. The peroxides were obtained in purities ranging from 98-100%, after one recrystallization, as determined by iodometric titration.

The 5-methyl bis(2-thenoyl) peroxide was prepared by the reaction of 5-methyl-2-thenoyl chloride with sodium perthenoate (4, 38). The peroxide partially decomposed and took on a slight yellow coloration after storage in a vacuum dessicator, at 0°, for several months. The other peroxides remained colorless and showed no decomposition when stored at 0° for similar periods of time.

Several attempts at the preparation of bis(5-methoxy-2-thenoyl) peroxide were unsuccessful. This peroxide is unstable and decomposed spontaneously on exposure to the atmosphere.

While this investigation was in progress, Ford and Mackay (15) reported their studies on the decomposition of bis (2-thenoyl) peroxide in a variety of aromatic solvents. Their results indicated that the thenoate free-radical initially formed in the spontaneous decomposition of the bis(2-thenoyl) peroxide is considerably more stable towards decarboxylation than is the benzoate free-radical (see page 8). In the present study, it was found that very little carbon dioxide was evolved during the decomposition of bis(2-thenoyl) peroxide in carbon tetrachloride as a solvent. Of interest is the fact that under similar experimental conditions (see page 53) bis(3-thenoyl) peroxide evolved more than double the amount of carbon dioxide than did bis(2-thenoyl) peroxide. This indicates that the resonance stabilization of the 3-thenoate free-radical is much less than that of the 2-thenoate free-radical.





The product analysis determined with bis(2-thenoyl) peroxide in the absence of any free-radical inhibitor indicates that in the presence of a solvent lacking easily extractable hydrogen atoms, such as carbon tetrachloride, the thenoate radical preferentially attacks undecomposed peroxide molecules by abstracting a hydrogen atom to yield 2-thenoic acid (16% of theory). This would account for the rapid initial rate of its decomposition, which gradually decreases as the concentration of unreacted peroxide diminishes (see Figure X). The dark colored amorphous material, which was isolated in yields of 46% by weight, is probably formed from the peroxide molecules attacked by the initially formed thenoate free-radicals. Elementary analysis (see page 51) of the amorphous material corresponded to neither polythienyl thenoate nor polythienyl. The material was not further investigated.

The presence of either 0.20 M styrene, or 0.20 M 3,4-dichlorostyrene markedly lowered the rate of decomposition of bis(2-thenoyl) peroxide (cf. Figures I and X). Furthermore, at the end of the kinetic runs the sample solutions were colorless as contrasted to the brown coloration in the absence of an inhibitor. Styrene was found to be an effective inhibitor, while 3,4-dichlorostyrene is probably an even more efficient inhibitor (see Figure XIII on the kinetics of the decomposition of bis(5-nitro-2-thenoyl) peroxide). The increased polarity of the chlorinated styrene probably makes it more succeptible to electrophilic attack by thenoate radicals and thus more efficient in eliminating the induced decomposition.

All kinetic determinations were carried out in carbon tetrachloride containing 0.20 M 3,4-dichlorostyrene. Some preliminary studies were made using 0.20 M styrene as the inhibitor. The peroxide concentrations varied from 0.0090 M to 0.025 M. The rates of thermal decomposition of the bis (thenoyl) peroxides were found to obey the first order rate equation,

$$-\frac{dC}{dt} = kC; \qquad (1)$$

which on integration gives,

$$k = \frac{2.303}{t} \log \frac{C_o}{C} \qquad (2)$$

where C is the concentration of peroxide at time t, C_o is the initial concentration of peroxide and k is the first order rate constant. The rate constants were calculated from the slope (47) of the plots of log C versus t (see Figure I for a typical plot), the slope in each case having been determined by the method of least squares.

The activation energies, E_a, were calculated using the Arrhenius equation,

$$\log k = \frac{E_a}{2.303R} \frac{1}{T}$$

where R is 1.987 calories degree^{-1} mole^{-1}, the gas law constant. The E_a values were estimated from the slope of the plots of log k versus 1/T (see Figures XIV-XXII).

The rate constants calculated at each point (equation 2) were used to determine the standard deviations (48). The rate constants for the thermal decomposition of the thenoyl peroxides, determined at 75°, in carbon tetrachloride are,

Peroxide	$k \times 10^3$ (min.$^{-1}$)
Bis(5-methyl-2-thenoyl)	2.54
Bis(5-t-butyl-2-thenoyl)	2.43
5-Methyl bis(2-thenoyl)	1.79
Bis(4-methyl-2-thenoyl)	1.76
Bis(2-thenoyl)	1.33
Bis(3-thenoyl)	1.29
Bis(5-chloro-2-thenoyl)	0.95
Bis(5-bromo-2-thenoyl)	0.92
Bis(4-bromo-2-thenoyl)	0.69

Examination of the rate constants show that the presence of electron donating substituents on the heterocyclic ring accelerate the rate of decomposition of the peroxide, while electron withdrawing substituents have the opposite effect. These results are similar to those reported (4, 11) for the benzene analogs of these peroxides. The first order rate constants for the thermal decomposition of several substituted benzoyl peroxides, determined at 80°, in a dioxane medium containing 0.20 M 3,4-dichlorostyrene as the inhibitor as reported by Swain, Stockmayer and Clarke (4) are shown on page 69. The $(\sigma_1+\sigma_2)$ values listed are the sums of the substituent constants for the groups on the benzene ring of the peroxide (see page 1).

Peroxide	k x 10^3 (min.$^{-1}$)	$\sigma_1+\sigma_2$
Bis(p-methyl) benzoyl	3.68	-0.340
Bis(p-*t*-butyl) benzoyl	3.65	-0.394
Bis(m-methyl) benzoyl	2.64	-0.138
Bis(benzoyl)	2.52	0.000
Bis(p-chloro) benzoyl	2.17	-0.454
Bis(p-bromo) benzoyl	1.94	-0.464
Bis(m-bromo) benzoyl	1.54	-0.782

When the values of log k/k_0 were plotted against $(\sigma_1+\sigma_2)$, a fairly good straight line resulted. Thus, it has been demonstrated that the Hammett equation is applicable to the spontaneous decomposition of substituted bis(benzoyl) peroxides. However, the linear relationship is only approximate, since the frequency factor as well as the activation energy was found to be affected by a change of substituent.

There is a close parallel in rate constants, both in the absolute values and the relative order for the corresponding thenoyl and benzoyl peroxides, if the reasonable assumption is made that the 5-substituted thenoyl peroxides are analogous to the para-substituted benzoyl peroxides. As the rate constants for the benzoyl peroxides were determined at 80° while those for the thenoyl peroxides were determined at 75°, a better comparison between the two series of peroxides can be made by doubling the recorded rate constants for the thenoyl peroxides, since in the latter case the rate constant doubles, roughly, for each five degree rise in the decomposition temperature.

When the values of log k/k_0 for the bis(2-thenoyl) peroxides were plotted against $(\sigma_1+\sigma_2)$, a fairly good straight line resulted for the 4- and 5-substituted thenoyl peroxides studied. The assumption was made that the σ values derived from the ionization constants of the substituted benzoic acids are reasonably applicable to the corresponding thiophene analogs.

The value of the reaction constant, ρ , is equal to -0.38 for the benzoyl peroxides. The small magnitude of this value shows that the electronic effect of the substituents has only a very small influence on the rate of decomposition of the benzoyl peroxides. The reaction constant, ρ , for the bis(2-thenoyl) peroxides is -0.44 (see Figure XXIII), and is approximately equal to the ρ value for the substituted benzoyl peroxides.

The activation energies for the decomposition of the bis (2-thenoyl) peroxides are all of the same magnitude, 29.5 ± 1.0 kilocalories per mole (slopes of Figures XIV-XXII). The relative constancy of the activation energy throughout the entire range of substituents would seem to indicate an insensitivity of the rate of decomposition to the electron withdrawing or electron releasing power of the substituents. However, the rate constants themselves do show a definite dependence on the electronic character of the particular substituent. Thus, it appears reasonable to conclude that the frequency factor must vary with a change in substituents, and the Hammett relationship can only be approximate when applied to an interpretation of the rates of decomposition of the substituted bis(2-thenoyl) peroxides.

SUMMARY

1. Ten previously unreported bis(2-thenoyl) peroxides were prepared. Three new intermediate thenoyl chlorides were also synthesized.

2. The rates of decomposition of the bis(2-thenoyl) peroxides were determined. All of the kinetic studies were carried out in dilute carbon tetrachloride solution in the presence of 3,4-dichlorostyrene as a free-radical scavenger. The decompositions all followed strict first order kinetics, with the exception of bis(5-nitro-2-thenoyl) peroxide. The rate constants as determined at 75° are:

Peroxide	k x 10^3 (min.$^{-1}$)
Bis(5-methyl-2-thenoyl)	2.54
Bis(5-t-butyl-2-thenoyl)	2.43
5-Methyl bis(2-thenoyl)	1.79
Bis(4-methyl-2-thenoyl)	1.76
Bis(2-thenoyl)	1.33
Bis(3-thenoyl)	1.29
Bis(5-chloro-2-thenoyl)	0.95
Bis(5-bromo-2-thenoyl)	0.92
Bis(4-bromo-2-thenoyl)	0.69

3. Activation energies were determined and found to be 29.5 ± 1.0 kilocalories per mole for all the peroxides studied.

The Hammett equation was found to be applicable to the decomposition of the peroxides. However, the fact that the rate constants show a definite dependence on the electronic character of the particular substituent, while the activation energies are relatively constant over the entire range of substituents, indicates that the frequency factor must vary with a change in substituent and therefore the Hammett relationship can only be approximate for the decomposition of the bis(2-thenoyl) peroxides.

APPENDIX

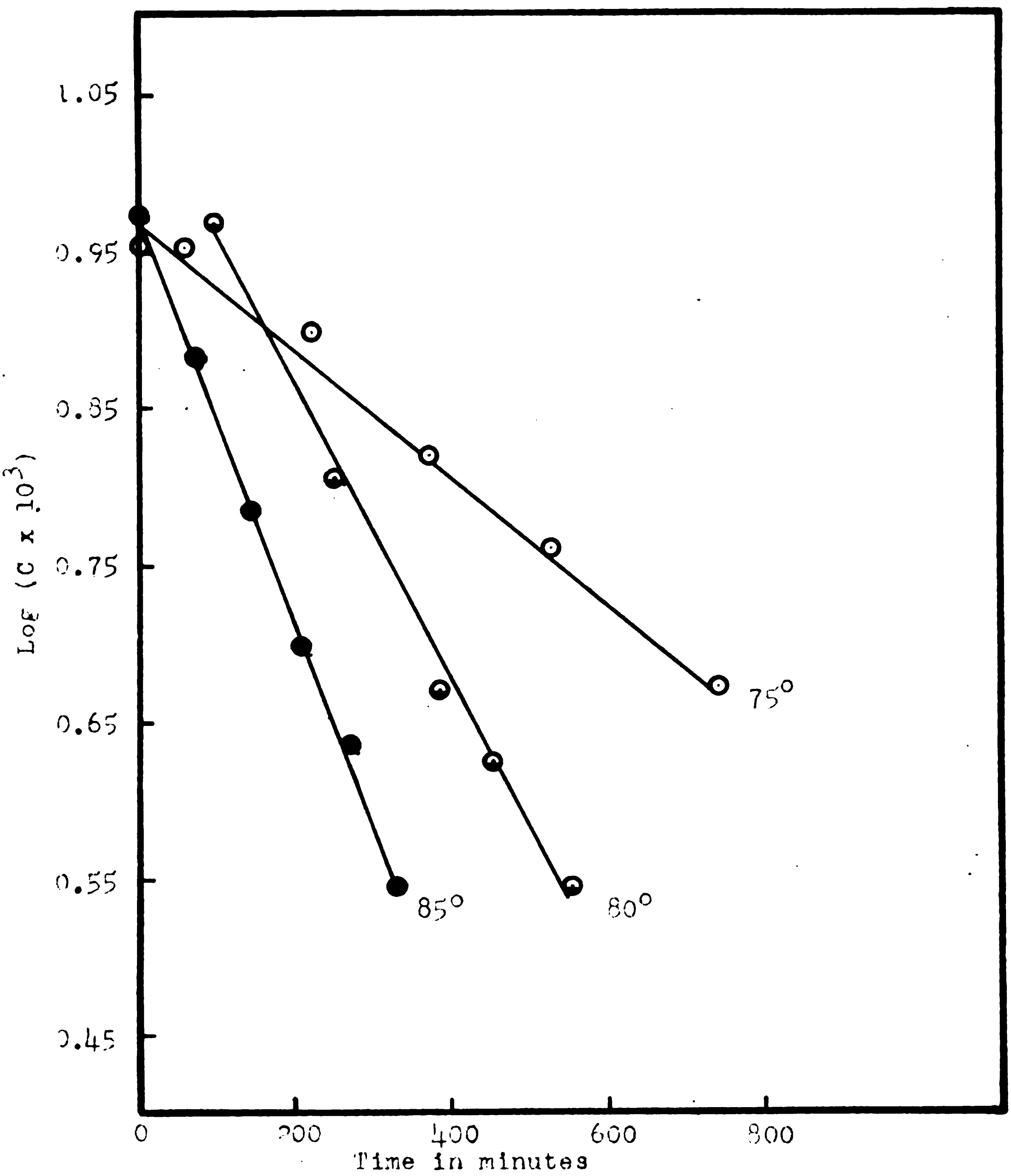


Figure II. Log peroxide concentration versus time for the decomposition of bis(5-bromo-2-thenoyl) peroxide in carbon tetrachloride in the presence of 0.20 M 3,4-dichlorostyrene at 75°, 80° and 85°.

TABLE 7

DECOMPOSITION OF BIS(5-BROMO-2-THENOYL) PEROXIDE IN THE PRESENCE OF 0.20 M 3,4-DICHLOROSTYRENE IN CARBON TETRACHLORIDE AT 75°

ml. = milliliters of 0.01109 N sodium thiosulfate

C = molarity of peroxide solution

t = time in minutes

Sample	ml.	$C \times 10^3$	$\log (C \times 10^3)$	t
1	8.12	9.005	0.95448	0
2	8.09	8.972	0.95289	70
3	7.14	7.918	0.89862	220
4	5.96	6.610	0.82020	370
5	5.21	5.778	0.76178	525
6	4.25	4.713	0.67330	735

$k = 9.23 \pm 1.47 \times 10^{-4}$

TABLE 8

DECOMPOSITION OF BIS(5-BROMO-2-THENOYL) PEROXIDE IN THE PRESENCE OF 0.20 M 3,4-DICHLOROSTYRENE IN CARBON TETRACHLORIDE AT 80°

ml. = milliliters of 0.01109 N Sodium thiosulfate

C = molarity of peroxide solution

t = time in minutes

Sample	ml.	$C \times 10^3$	$\log (C \times 10^3)$	t
1	8.42	9.338	0.97025	95
2	5.76	6.388	0.80536	245
3	4.21	4.669	0.66922	380
4	3.81	4.225	0.62583	445
5	3.16	3.504	0.54456	545

$k = 2.18 \pm \quad \times 10^{-3}$

TABLE 9

DECOMPOSITION OF BIS(5-BROMO-2-THENOYL) PEROXIDE IN THE PRESENCE OF 0.20 M 3,4-DICHLOROSTYRENE IN CARBON TETRACHLORIDE AT 85°

ml. = milliliters of 0.01109 N sodium thiosulfate

C = molarity of peroxide solution

t = time in minutes

Sample	ml.	$C \times 10^3$	$\log (C \times 10^3)$	t
1	8.48	9.404	0.97331	0
2	6.90	7.6521	0.88377	70
3	5.51	6.111	0.78611	140
4	4.50	4.991	0.69819	200
5	3.90	4.325	0.63599	260
6	3.18	3.527	0.54741	320

$k = 3.08 \pm .08 \times 10^{-3}$

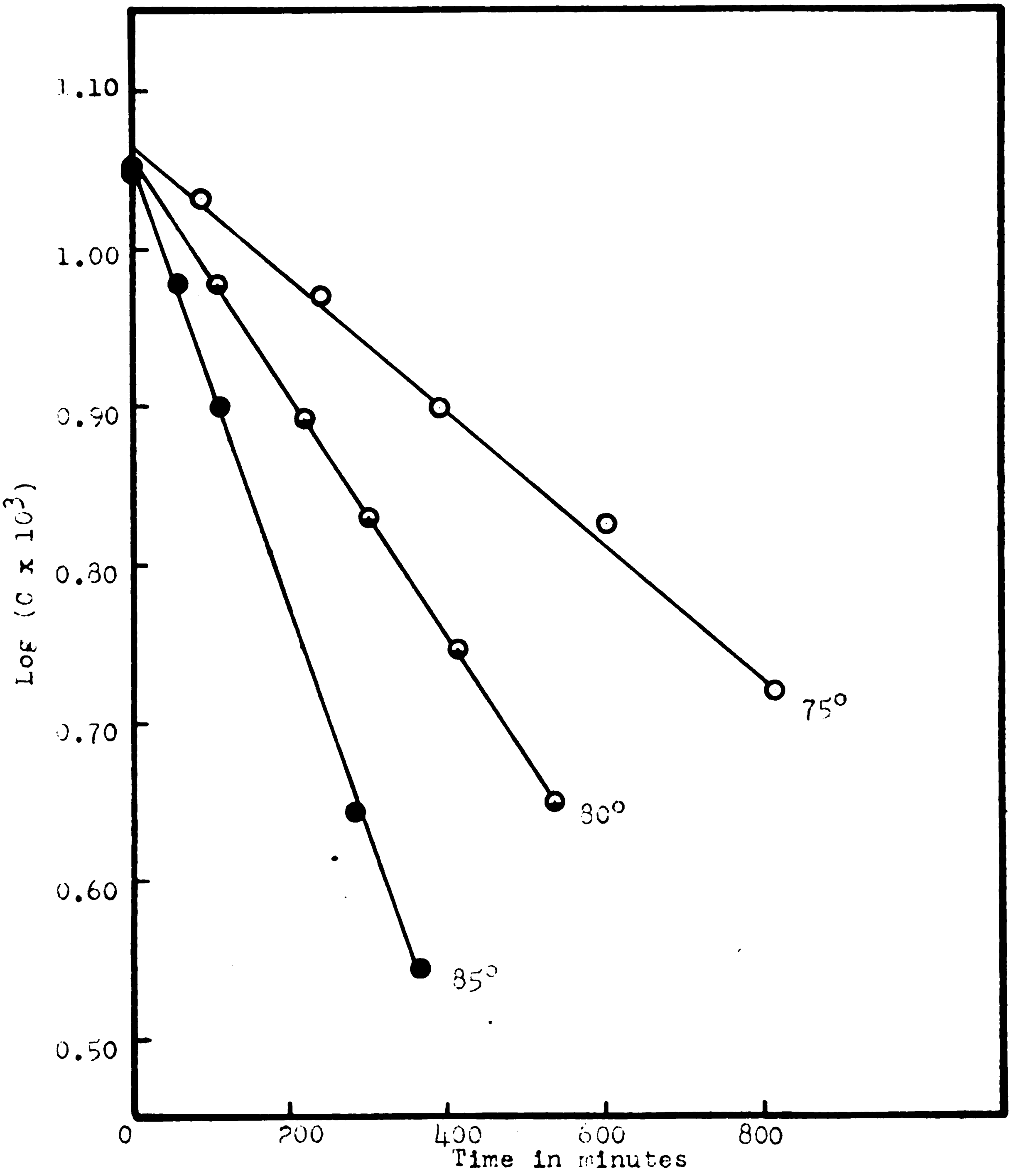


Figure III. Log peroxide concentration versus time for the decomposition of bis(5-chloro-2-thenoyl) peroxide in carbon tetrachloride in the presence of 0.20 M 3,4-dichlorostyrene at 75°, 80° and 85°.

TABLE 10

DECOMPOSITION OF BIS(5-CHLORO-2-THENOYL) PEROXIDE IN THE PRESENCE OF 0.20 M 3,4-DICHLOROSTYRENE IN CARBON TETRACHLORIDE AT 75°

ml. = milliliters of 0.009535 N sodium thiosulfate

C = molarity of peroxide solution

t = time in minutes

Sample	ml.	$C \times 10^3$	$\log (C \times 10^3)$	t
1	11.71	11.17	1.04805	0
2	11.31	10.78	1.03262	90
3	9.80	9.344	0.97053	240
4	8.33	7.943	0.89998	390
5	7.03	6.703	0.82627	600
6	5.49	5.235	0.71892	810

$k = 9.46 \pm 1.96 \times 10^{-4}$

TABLE 11

DECOMPOSITION OF BIS(5-CHLORO-2-THENOYL) PEROXIDE IN THE PRESENCE OF 0.20 M 3,4-DICHLOROSTYRENE IN CARBON TETRACHLORIDE AT 80°

ml. = milliliters of 0.009535 N sodium thiosulfate

C = molarity of peroxide solution

t = time in minutes

Sample	ml.	$C \times 10^3$	$\log (C \times 10^3)$	t
1	11.73	11.18	1.04844	0
2	9.95	9.487	0.97713	110
3	8.19	7.809	0.89260	220
4	7.08	6.751	0.82937	310
5	5.85	5.578	0.74648	410
6	4.69	4.472	0.65050	530

$k = 1.74 \pm .09 \times 10^{-3}$

TABLE 12

DECOMPOSITION OF BIS(5-CHLORO-2-THENOYL) PEROXIDE IN THE PRESENCE OF 0.20 M 3,4-DICHLOROSTYRENE IN CARBON TETRACHLORIDE AT 85°

ml. = milliliters of 0.009535 N sodium thiosulfate

C = molarity of peroxide solution

t = time in minutes

Sample	ml.	$C \times 10^3$	$\log (C \times 10^3)$	t
1	11.78	11.23	1.05038	0
2	9.97	9.506	0.97800	60
3	8.33	7.943	0.89998	110
4	4.61	4.396	0.64296	280
5	3.69	3.518	0.54630	360

$k = 3.30 \pm .46 \times 10^{-3}$

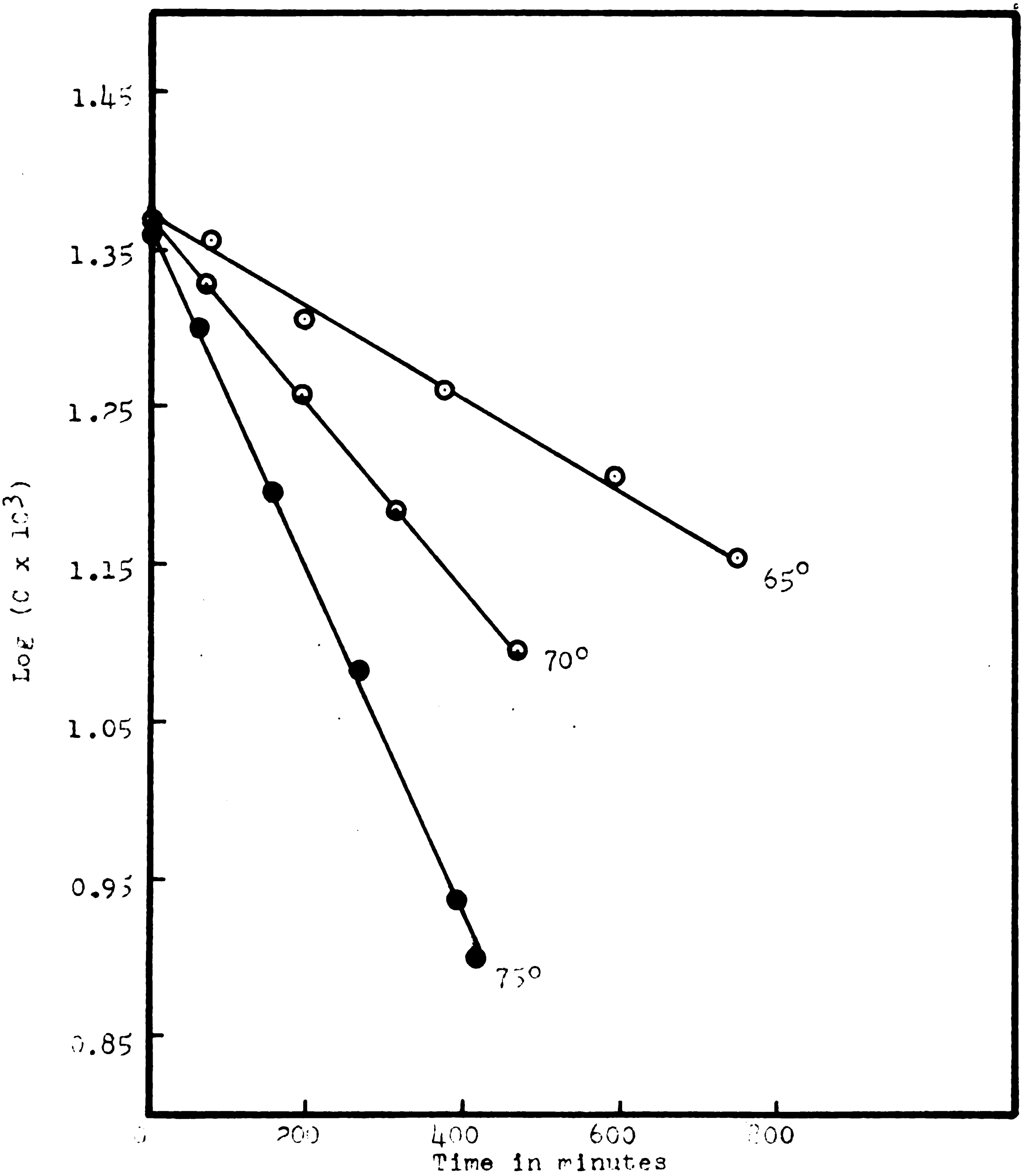


Figure IV. Log peroxide concentration versus time for the decomposition of bis(5-methyl-2-thenoyl) peroxide in carbon tetrachloride in the presence of 0.20 M 3,4-dichlorostyrene at 65°, 70°, and 75°.

TABLE 13

DECOMPOSITION OF BIS(5-METHYL-2-THENOYL) PEROXIDE IN THE PRESENCE OF 0.20 M 3,4-DICHLOROSTYRENE IN CARBON TETRACHLORIDE AT 65°

ml. = milliliters of 0.01109 N sodium thiosulfate

C = molarity of peroxide solution

t = time in minutes

Sample	ml.	$C \times 10^3$	$\log (C \times 10^3)$	t
1	24.49	23.35	1.36829	0
2	23.80	22.69	1.35583	75
3	21.95	20.93	1.30942	195
4	19.14	18.25	1.26126	375
5	16.84	16.06	1.20575	590
6	14.95	14.25	1.15381	745

$k = 6.63 \pm 1.05 \times 10^{-4}$

TABLE 14

DECOMPOSITION OF BIS(5-METHYL-2-THENOYL) PEROXIDE IN THE PRESENCE OF 0.20 M 3,4-DICHLOROSTYRENE IN CARBON TETRACHLORIDE AT 70°

ml. = milliliters of 0.01109 N sodium thiosulfate

C = molarity of peroxide solution

t = time in minutes

Sample	ml.	$C \times 10^3$	$\log (C \times 10^3)$	t
1	21.00	23.29	1.36717	0
2	19.18	21.28	1.32797	70
3	16.32	18.10	1.25768	190
4	13.82	15.33	1.18554	310
5[a]	11.24	12.47	1.09587	465
6[a]	11.39	12.63	1.10140	465

$k = 1.33 \pm .02 \times 10^{-3}$

[a] Duplicate samples

TABLE 15

DECOMPOSITION OF BIS(5-METHYL-2-THENOYL) PEROXIDE IN THE PRESENCE OF 0.20 M 3,4-DICHLOROSTYRENE IN CARBON TETRACHLORIDE AT 75°

ml. = milliliters of 0.01109 N sodium thiosulfate

C = molarity of peroxide solution

t = time in minutes

Sample	ml.	$C \times 10^3$	$\log (C \times 10^3)$	t
1	20.64	22.89	1.35965	0
2	17.89	19.84	1.29754	60
3	14.15	15.69	1.19562	155
4	10.91	12.10	1.08279	265
5	7.76	8.606	0.93480	390
6	7.13	7.907	0.89801	415

$k = 2.54 \pm .06 \times 10^{-3}$

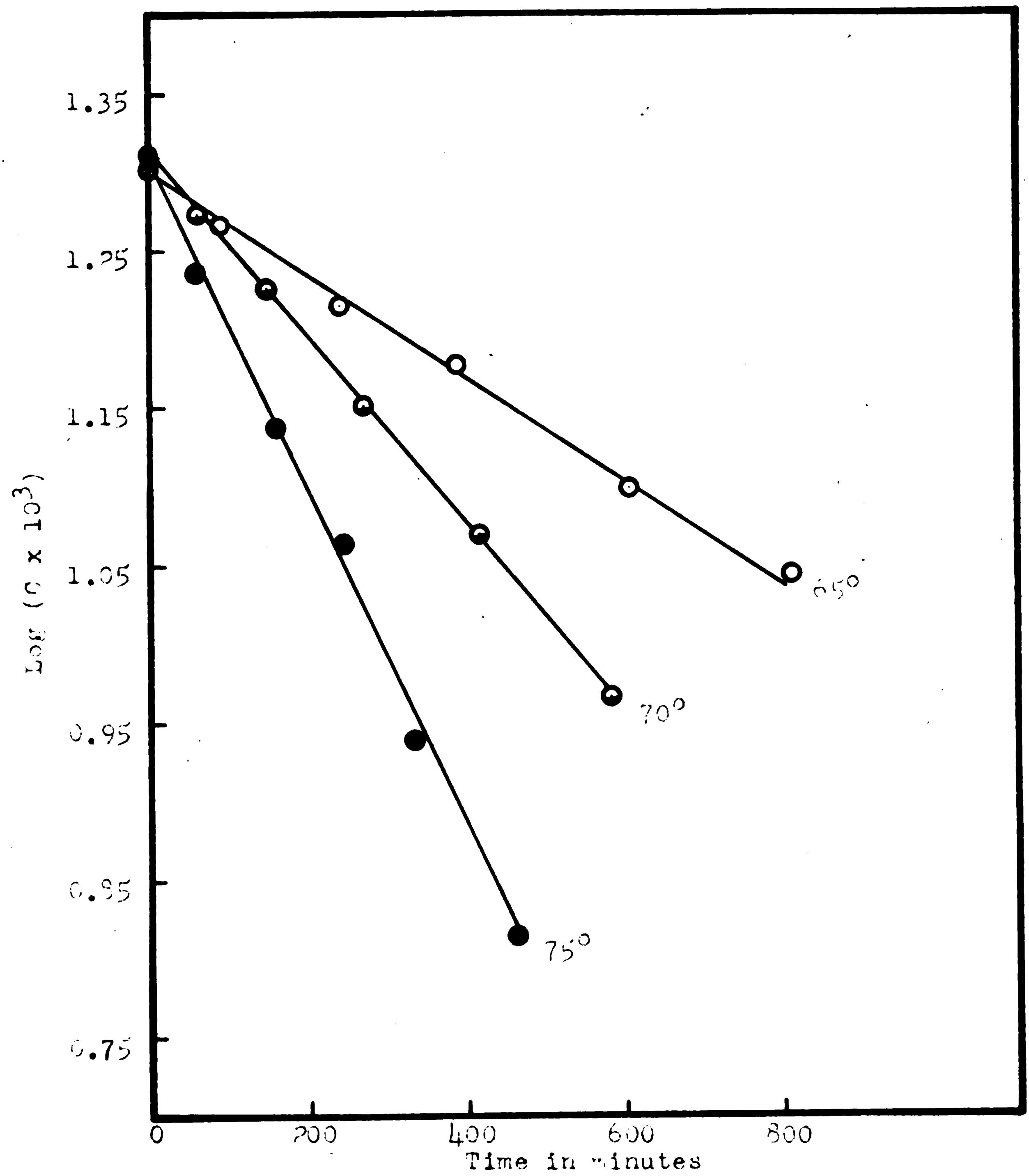


Figure V. Log peroxide concentration versus time for the decomposition of bis(5-*t*-butyl-2-thenoyl) peroxide in carbon tetrachloride in the presence of 0.20 M 3,4-dichlorostyrene at 65°, 70° and 75°.

TABLE 16

DECOMPOSITION OF BIS(5-t-BUTYL-2-THENOYL) PEROXIDE IN THE PRESENCE OF 0.20 M 3,4-DICHLOROSTYRENE IN CARBON TETRACHLORIDE AT 65°

ml. = milliliters of 0.009535 N sodium thiosulfate

C = molarity of peroxide solution

t = time in minutes

Sample	ml.	$C \times 10^3$	$\log (C \times 10^3)$	t
1	20.97	19.99	1.30081	0
2	19.40	18.50	1.26717	90
3	17.22	16.42	1.21537	240
4	15.80	15.07	1.17811	390
5	13.20	12.59	1.10003	610
6	11.62	11.08	1.04454	815

$k = 7.36 \pm .53 \times 10^{-4}$

TABLE 17

DECOMPOSITION OF BIS(5-t-BUTYL-2-THENOYL) PEROXIDE IN THE PRESENCE OF 0.20 M 3,4-DICHLOROSTYRENE IN CARBON TETRACHLORIDE AT 70°

ml. = milliliters of 0.01109 N sodium thiosulfate

C = molarity of peroxide solution

t = time in minutes

Sample	ml.	$C \times 10^3$	$\log (C \times 10^3)$	t
1	18.40	20.41	1.30984	0
2	16.92	18.76	1.27323	60
3	15.25	16.91	1.22814	150
4	12.79	14.18	1.15168	270
5	10.60	11.76	1.07041	420
6	8.36	9.271	0.96713	585

$k = 1.33 \pm .19 \times 10^{-3}$

TABLE 18

DECOMPOSITION OF BIS(5-t-BUTYL-2-THENOYL) PEROXIDE IN THE PRESENCE OF 0.20 M 3,4-DICHLOROSTYRENE IN CARBON TETRACHLORIDE AT 75°

ml. = milliliters of 0.01109 N sodium thiosulfate

C = molarity of peroxide solution

t = time in minutes

Sample	ml.	$C \times 10^3$	$\log (C \times 10^3)$	t
1	18.26	20.25	1.30643	0
2	15.52	17.21	1.23578	60
3	12.41	13.76	1.13862	160
4	10.47	11.61	1.06483	245
5	7.84	8.695	0.93927	335
6	5.90	6.543	0.81578	465

$k = 2.43 \pm .11 \times 10^{-3}$

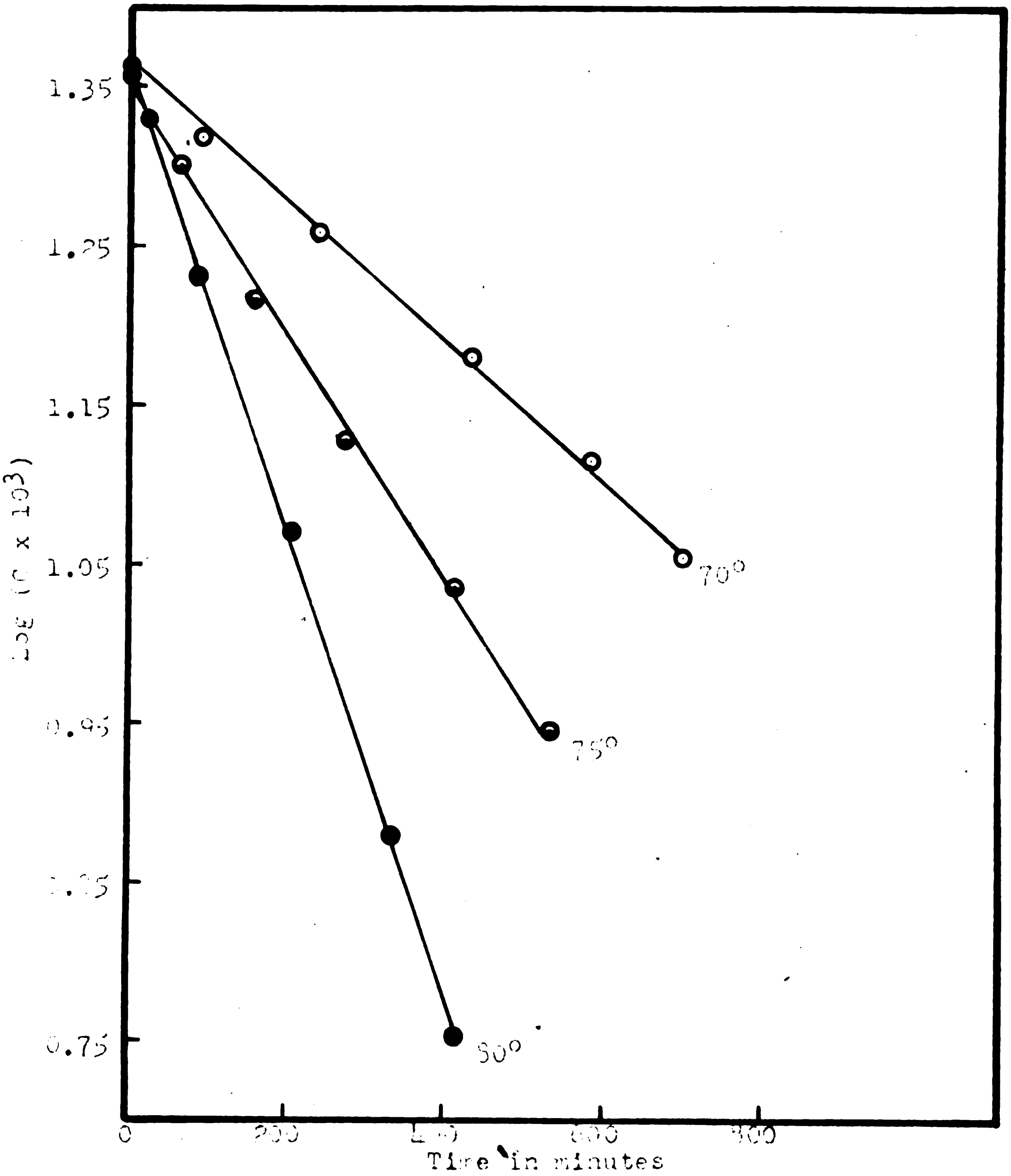


Figure VI. Log peroxide concentration versus time for the decomposition of bis(4-methyl-2-thenoyl) peroxide in carbon tetrachloride in the presence of 0.20 M 3,4-dichlorostyrene at 70°, 75° and 80°.

TABLE 19

DECOMPOSITION OF BIS(4-METHYL-2-THENOYL) PEROXIDE IN THE PRESENCE OF 0.20 M 3,4-DICHLOROSTYRENE IN CARBON TETRACHLORIDE AT 70°

ml. = milliliters of 0.01109 N sodium thiosulfate

C = molarity of peroxide solution

t = time in minutes

Sample	ml.	$C \times 10^3$	$\log(C \times 10^3)$	t
1	20.50	22.73	1.35660	0
2	18.78	20.83	1.31869	95
3	16.33	18.11	1.25792	240
4	13.64	15.13	1.17984	435
5	11.76	13.04	1.11528	585
6	10.27	11.39	1.05652	700

$k = 9.77 \pm .22 \times 10^{-4}$

TABLE 20

DECOMPOSITION OF BIS(4-METHYL-2-THENOYL) PEROXIDE IN THE PRESENCE OF 0.20 M 3,4-DICHLOROSTYRENE IN CARBON TETRACHLORIDE AT 75°

ml. = milliliters of 0.01109 N sodium thiosulfate

C = molarity of peroxide solution

t = time in minutes

Sample	ml.	$C \times 10^3$	$\log (C \times 10^3)$	t
1	20.47	22.70	1.35603	0
2	18.00	19.96	1.30016	70
3	14.87	16.49	1.21722	160
4	12.11	13.43	1.12808	275
5	9.79	10.86	1.03583	415
6	7.95	8.817	0.94532	535

$k = 1.76 \pm .09 \times 10^{-3}$

TABLE 21

DECOMPOSITION OF BIS(4-METHYL-2-THENOYL) PEROXIDE IN THE PRESENCE OF 0.20 M 3,4-DICHLOROSTYRENE IN CARBON TETRACHLORIDE AT 80°

ml. = milliliters of 0.01109 N sodium thiosulfate

C = molarity of peroxide solution

t = time in minutes

Sample	ml.	$C \times 10^3$	$\log (C \times 10^3)$	t
1	20.83	23.10	1.36361	0
2	19.24	21.34	1.32919	25
3	15.32	16.99	1.23019	90
4	10.63	11.79	1.07151	210
5	6.81	7.552	0.87806	335
6	5.11	5.667	0.75335	415

$k = 3.37 \pm .09 \times 10^{-3}$

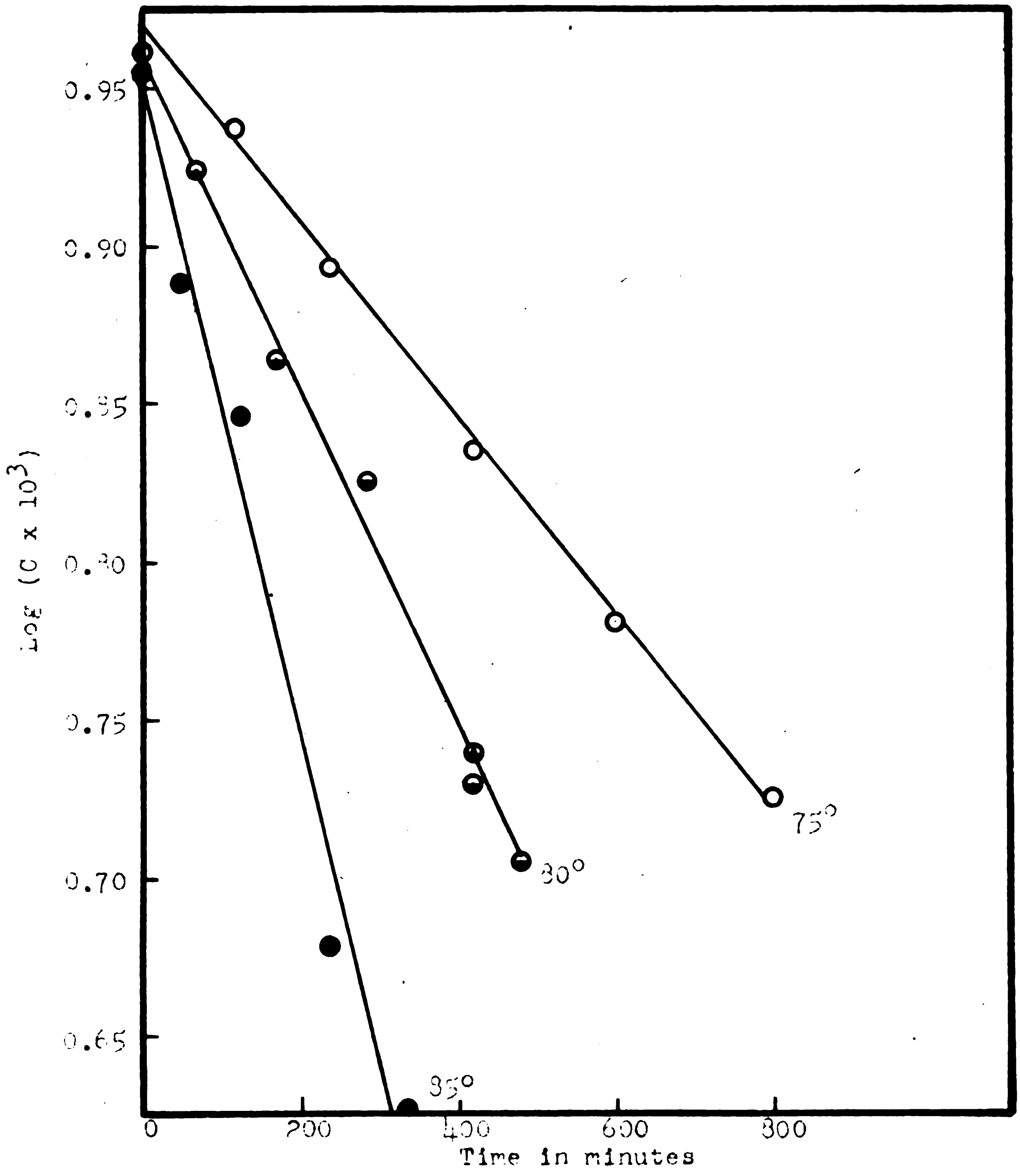


Figure VII. Log peroxide concentration versus time for the decomposition of bis(4-bromo-2-thenoyl) peroxide in carbon tetrachloride in the presence of 0.20 M 3,4-dichlorostyrene at 75°, 80° and 85°.

TABLE 22

DECOMPOSITION OF BIS(4-BROMO-2-THENOYL) PEROXIDE IN THE PRESENCE OF 0.20 M 3,4-DICHLOROSTYRENE IN CARBON TETRACHLORIDE AT 75°

ml. = milliliters of 0.009535 N sodium thiosulfate

C = molarity of peroxide solution

t = time in minutes

Sample	ml.	$C \times 10^3$	$\log (C \times 10^3)$	t
1[a]	9.53	9.087	0.95842	0
2[a]	9.54	9.096	0.95885	0
3	9.08	8.658	0.93742	120
4	8.19	7.809	0.89260	240
5	7.19	6.856	0.83607	420
6[b]	6.33	6.035	0.78068	600
7[b]	6.34	6.045	0.78140	600
8	5.58	5.321	0.72599	800

$k = 6.92 \pm .95 \times 10^{-4}$

[a, b] Duplicate samples

TABLE 23

DECOMPOSITION OF BIS(4-BROMO-2-THENOYL) PEROXIDE IN THE PRESENCE OF 0.20 M 3,4-DICHLOROSTYRENE IN CARBON TETRACHLORIDE AT 80°

ml. = milliliters of 0.009535 N sodium thiosulfate

C = molarity of peroxide solution

t = time in minutes

Sample	ml.	$C \times 10^3$	$\log (C \times 10^3)$	t
1[a]	9.58	9.135	0.96071	0
2[a]	9.56	9.115	0.95976	0
3	8.79	8.381	0.92330	70
4	7.67	7.313	0.86410	170
5	6.66	6.350	0.80277	235
6[b]	5.63	5.368	0.72981	420
7[b]	5.77	5.502	0.74052	420
8	5.32	5.073	0.70526	480

$k = 1.23 \pm .03 \times 10^{-3}$

[a,b] Duplicate samples

TABLE 24

DECOMPOSITION OF BIS(4-BROMO-2-THENOYL) PEROXIDE IN THE PRESENCE OF 0.20 M 3,4-DICHLOROSTYRENE IN CARBON TETRACHLORIDE AT 85°

ml. = milliliters of 0.009535 N sodium thiosulfate

C = molarity of peroxide solution

t = time in minutes

Sample	ml.	$C \times 10^3$	$\log (C \times 10^3)$	t
1	9.53	9.087	0.95842	0
2	8.12	7.742	0.88885	50
3	7.38	7.037	0.84739	125
4	5.00	4.768	0.67834	235
5	4.45	4.243	0.62767	335

$k = 2.35 \pm .73 \times 10^{-3}$

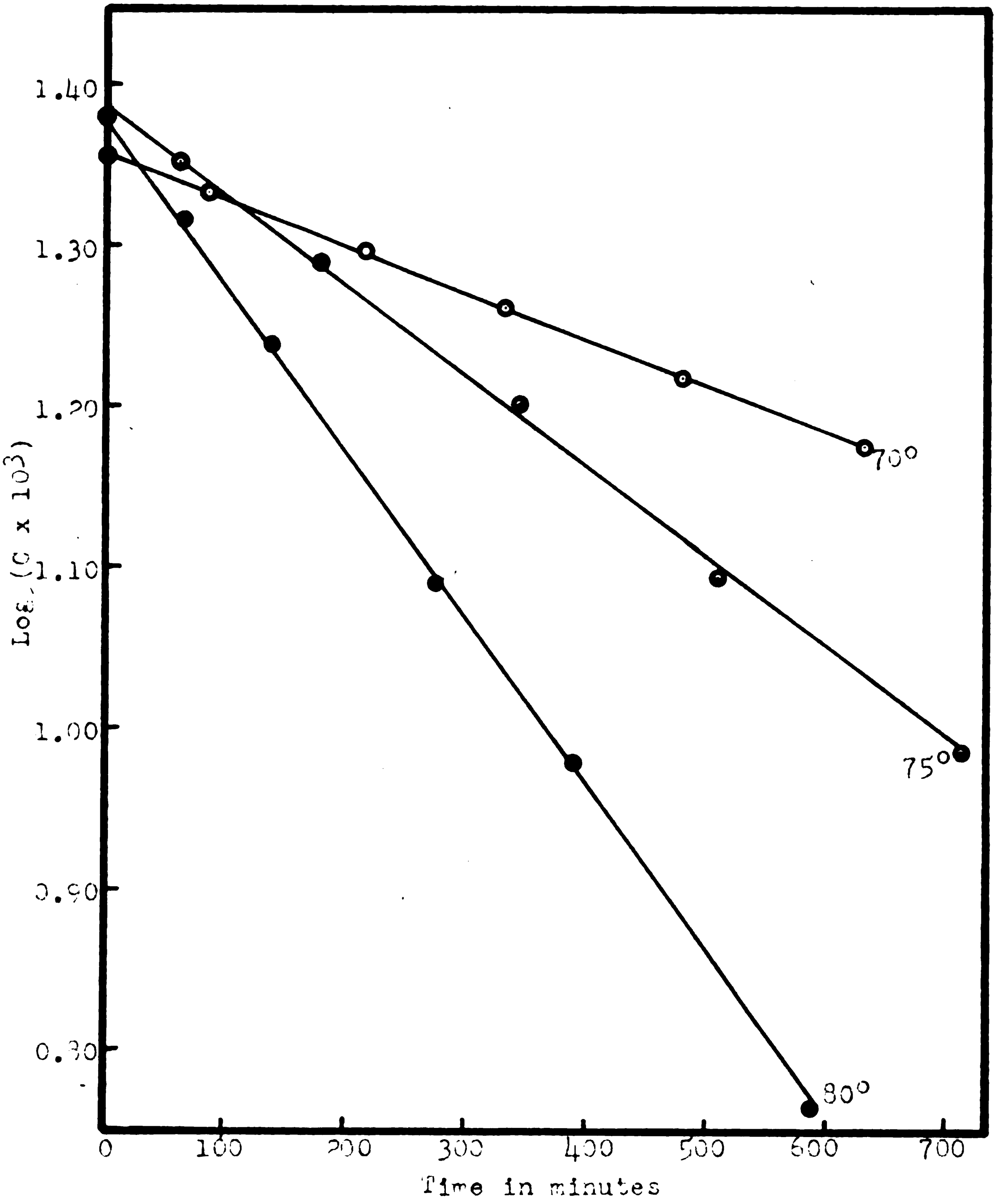


Figure VIII. Log peroxide concentration versus time for the decomposition of bis(3-thenoyl) peroxide in carbon tetrachloride in the presence of 0.20 M 3,4-dichlorostyrene at 70°, 75° and 80°

TABLE 25

DECOMPOSITION OF BIS(3-THENOYL) PEROXIDE IN THE PRESENCE OF 0.20 M 3,4-DICHLOROSTYRENE IN CARBON TETRACHLORIDE AT 70°

ml. = milliliters of 0.009905 N sodium thiosulfate

C = molarity of peroxide solution

t = time in minutes

Sample	ml.	$C \times 10^3$	$\log(C \times 10^3)$	t
1	23.20	22.98	1.36135	0
2	21.83	21.62	1.33486	90
3	20.08	19.89	1.28285	210
4	18.57	18.39	1.26458	330
5	16.80	16.64	1.22115	480
6[a]	16.92	16.76	1.22427	480
7	15.04	14.90	1.17319	630

$k = 6.65 \pm .06 \times 10^{-4}$

[a] Exposed to the air

TABLE 26

DECOMPOSITION OF BIS(3-THENOYL) PEROXIDE IN THE PRESENCE OF 0.20 M 3,4-DICHLOROSTYRENE IN CARBON TETRACHLORIDE AT 75°

ml. = milliliters of 0.009535 N sodium thiosulfate

C = molarity of peroxide solution

t = time in minutes

Sample	ml.	$C \times 10^3$	$\log (C \times 10^3)$	t
1	25.15	23.94	1.37912	0
2	23.78	22.67	1.35545	60
3	20.52	19.57	1.29159	180
4	16.77	15.99	1.20385	330
5	13.05	12.44	1.09482	510
6	10.19	9.716	0.98749	710

$k = 1.29 \pm .22 \times 10^{-3}$

TABLE 27

DECOMPOSITION OF BIS(3-THENOYL) PEROXIDE IN THE PRESENCE OF 0.20 M 3,4-DICHLOROSTYRENE IN CARBON TETRACHLORIDE AT 80°

ml. = milliliters of 0.009535 N sodium thiosulfate

C = molarity of peroxide solution

t = time in minutes

Sample	ml.	$C \times 10^3$	$\log (C \times 10^3)$	t
1	25.50	24.31	1.38578	0
2	21.76	20.75	1.31702	70
3	18.26	17.41	1.24080	140
4	13.03	12.42	1.09377	275
5[a]	10.05	9.583	0.98150	390
6[a]	9.94	9.478	0.97672	390
7	6.53	6.226	0.79421	585

$k = 2.36 \pm .06 \times 10^{-3}$

[a] Duplicate samples

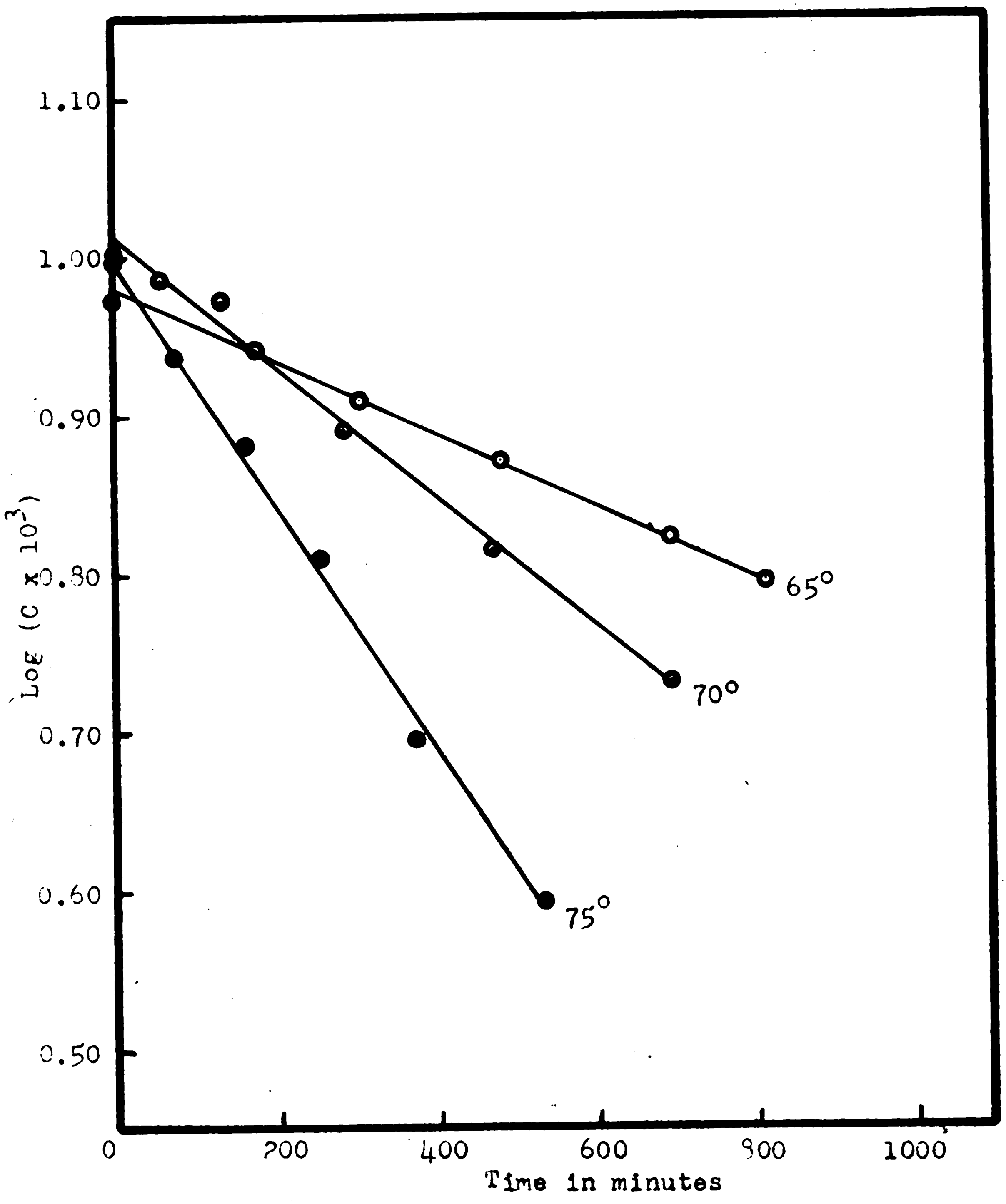


Figure IX. Log peroxide concentration versus time for the decomposition of 5-methyl bis(2-thenoyl) peroxide in carbon tetrachloride in the presence of 0.20 M 3,4-dichlorostyrene at 65°, 70° and 75°

TABLE 28

DECOMPOSITION OF 5-METHYL BIS(2-THENOYL) PEROXIDE IN THE PRESENCE OF 0.20 3,4-DICHLOROSTYRENE IN CARBON TETRACHLORIDE AT 65°

ml. = milliliters of 0.009905 N sodium thiosulfate

C = molarity of peroxide solution

t = time in minutes

Sample	ml.	$C \times 10^3$	$\log (C \times 10^3)$	t
1[a]	9.47	9.380	0.97220	0
2[a]	9.45	9.360	0.97128	0
3	9.45	9.360	0.97128	140
4	8.18	8.102	0.90859	310
5	7.48	7.409	0.86976	490
6[b]	6.70	6.636	0.82191	705
7[b]	6.66	6.596	0.81928	705
8	6.27	6.210	0.79309	820

$k = 5.19 - .80 \times 10^{-4}$

TABLE 29

DECOMPOSITION OF 5-METHYL BIS(2-THENOYL) PEROXIDE IN THE PRESENCE OF 0.20 M 3,4-DICHLOROSTYRENE IN CARBON TETRACHLORIDE AT 70°

ml. = milliliters of 0.01109 N sodium thiosulfate

C = molarity of peroxide solution

t = time in minutes

Sample	ml.	$C \times 10^3$	$\log (C \times 10^3)$	t
1	8.91	9.881	0.99480	0
2	8.69	9.637	0.98394	65
3	7.85	8.706	0.93928	185
4	7.00	7.763	0.89003	295
5	5.88	6.521	0.81431	480
6	4.84	5.368	0.73062	700

$k = 8.98 \pm 1.8 \times 10^{-4}$

TABLE 30

DECOMPOSITION OF 5-METHYL BIS(2-THENOYL) PEROXIDE IN THE PRESENCE OF 0.20 M 3,4-DICHLOROSTYRENE IN CARBON TETRACHLORIDE AT 75°

ml. = milliliters of 0.009535 N sodium thiosulfate

C = molarity of peroxide solution

t = time in minutes

Sample	ml.	$C \times 10^3$	$\log (C \times 10^3)$	t
1[a]	10.54	10.05	1.00217	0
2[a]	10.46	9.974	0.99887	0
3	9.07	8.648	0.93692	80
4	7.97	7.599	0.88076	170
5	6.74	6.427	0.80801	260
6[b]	5.20	4.958	0.69531	380
7[b]	5.17	4.929	0.69276	380
8	4.10	3.909	0.59207	540

$k = 1.79 \pm .09 \times 10^{-3}$

[a,b] Duplicate samples

TABLE 31

DECOMPOSITION OF BIS(2-THENOYL) PEROXIDE IN THE PRESENCE OF 0.20 M STYRENE IN CARBON TETRACHLORIDE AT 75°

ml. = milliliters of 0.00978 N sodium thiosulfate

C = molarity of peroxide solution

t = time in minutes

Sample	ml.	$C \times 10^3$	$\log (C \times 10^3)$	t
1	22.57	22.07	1.34380	70
2	18.33	17.93	1.25358	235
3[a]	14.13	13.82	1.14051	405
4	14.17	13.86	1.14176	405
5	12.93	12.65	1.10209	490
6[b]	13.00	12.71	1.10415	490

$k = 1.36 - \quad \times 10^{-3}$

[a] Glass wool added to ampoule

[b] Exposed to the air

TABLE 32

DECOMPOSITION OF BIS(5-t-BUTYL-2-THENOYL) PEROXIDE IN THE PRESENCE OF 0.20 M STYRENE IN CARBON TETRACHLORIDE AT 75°

ml. = milliliters of 0.00978 N sodium thiosulfate

C = molarity of peroxide solution

t = time in minutes

Sample	ml.	$C \times 10^3$	$\log (C \times 10^3)$	t
1	21.15	20.68	1.31555	0
2	18.56	18.15	1.25888	55
3	16.00	15.65	1.19451	115
4	11.38	11.13	1.04650	265
5	7.72	7.550	0.87795	445
6	6.17	6.030	0.78032	520

$k = 2.32 - .06 \times 10^{-3}$

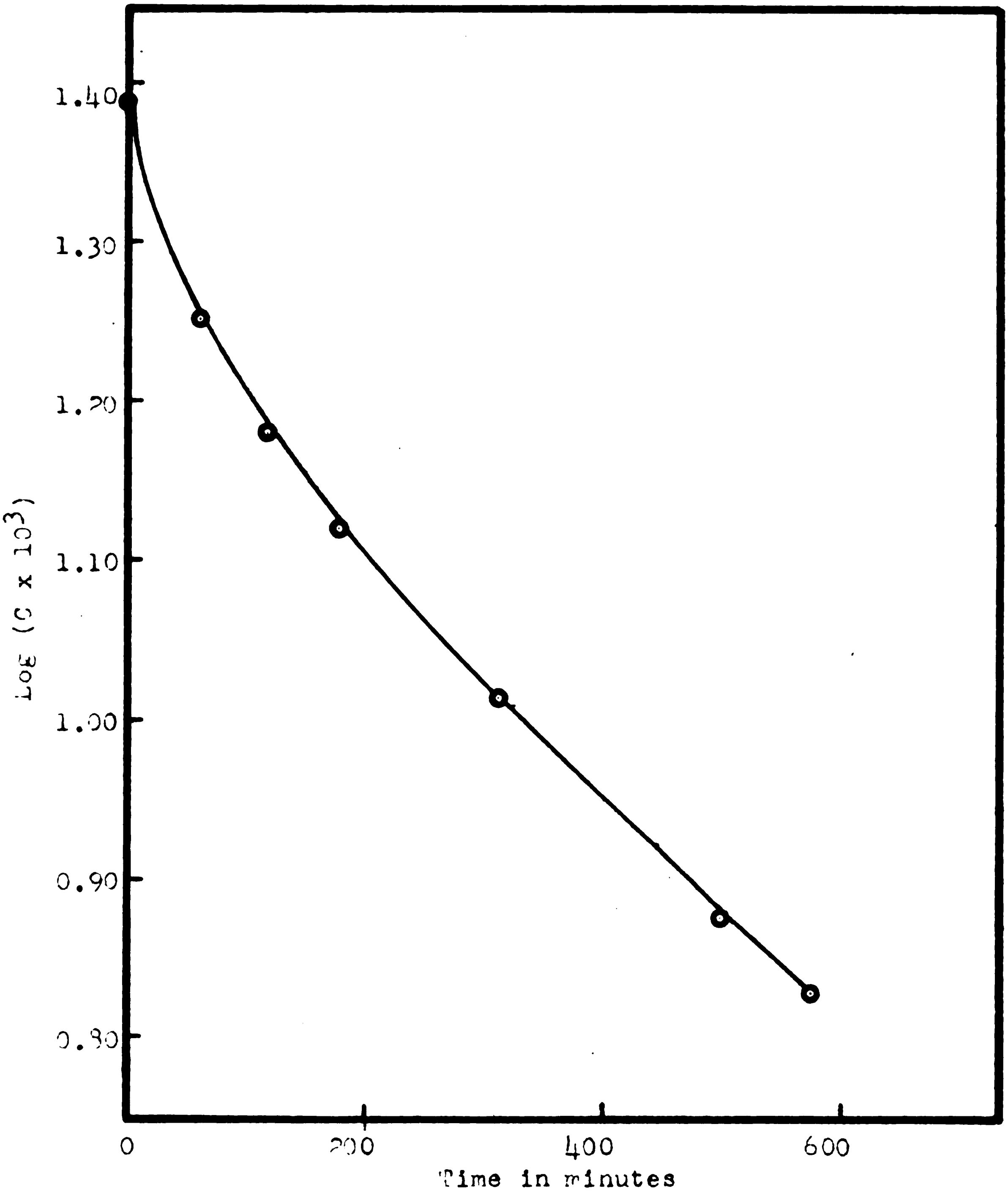


Figure X. Log peroxide concentration versus time for the decomposition of 0.025 M bis(2-thenoyl) peroxide in carbon tetrachloride in the absence of an inhibitor at 75°

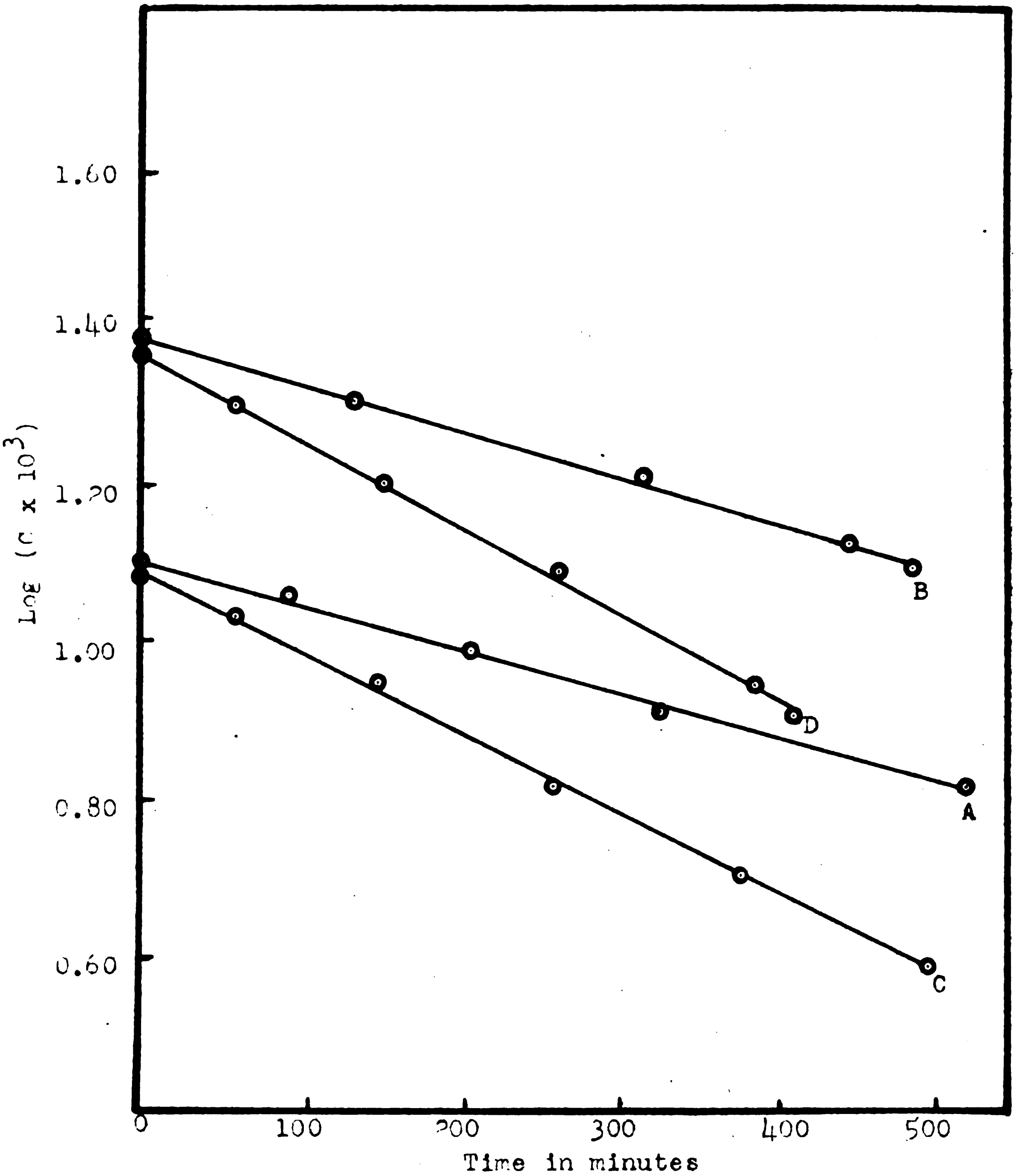


Figure XI. Log peroxide concentration versus time for different initial peroxide concentrations in carbon tetrachloride in the presence of 0.20 M 3,4-dichlorostyrene at 75°. A-0.01 M bis(2-thenoyl) peroxide, B-0.02 M bis (2-thenoyl) peroxide, C-0.01 M bis(5-methyl-2-thenoyl) peroxide, D-0.02 bis(5-methyl-2-thenoyl) peroxide

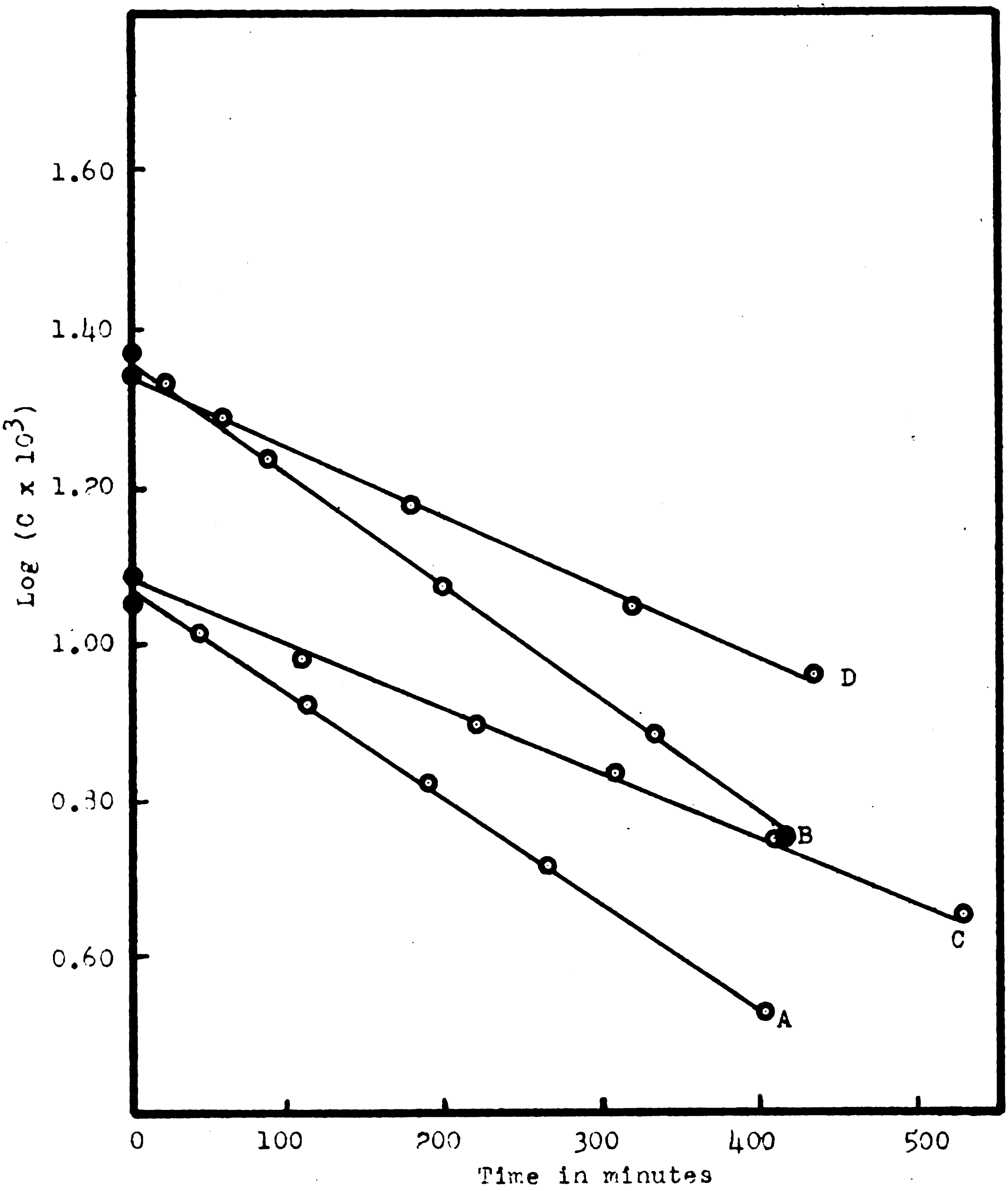


Figure XII. Log peroxide concentration versus time for different initial peroxide concentrations in carbon tetrachloride in the presence of 0.20 M 3,4-dichlorostyrene, at 80°. A-0.01 M bis(4-methyl-2-thenoyl) peroxide, B-0.02 M bis(4-methyl-2-thenoyl) peroxide, C-0.01 M bis (5-chloro-2-thenoyl) peroxide, D-0.02 M bis(5-chloro-2-thenoyl) peroxide

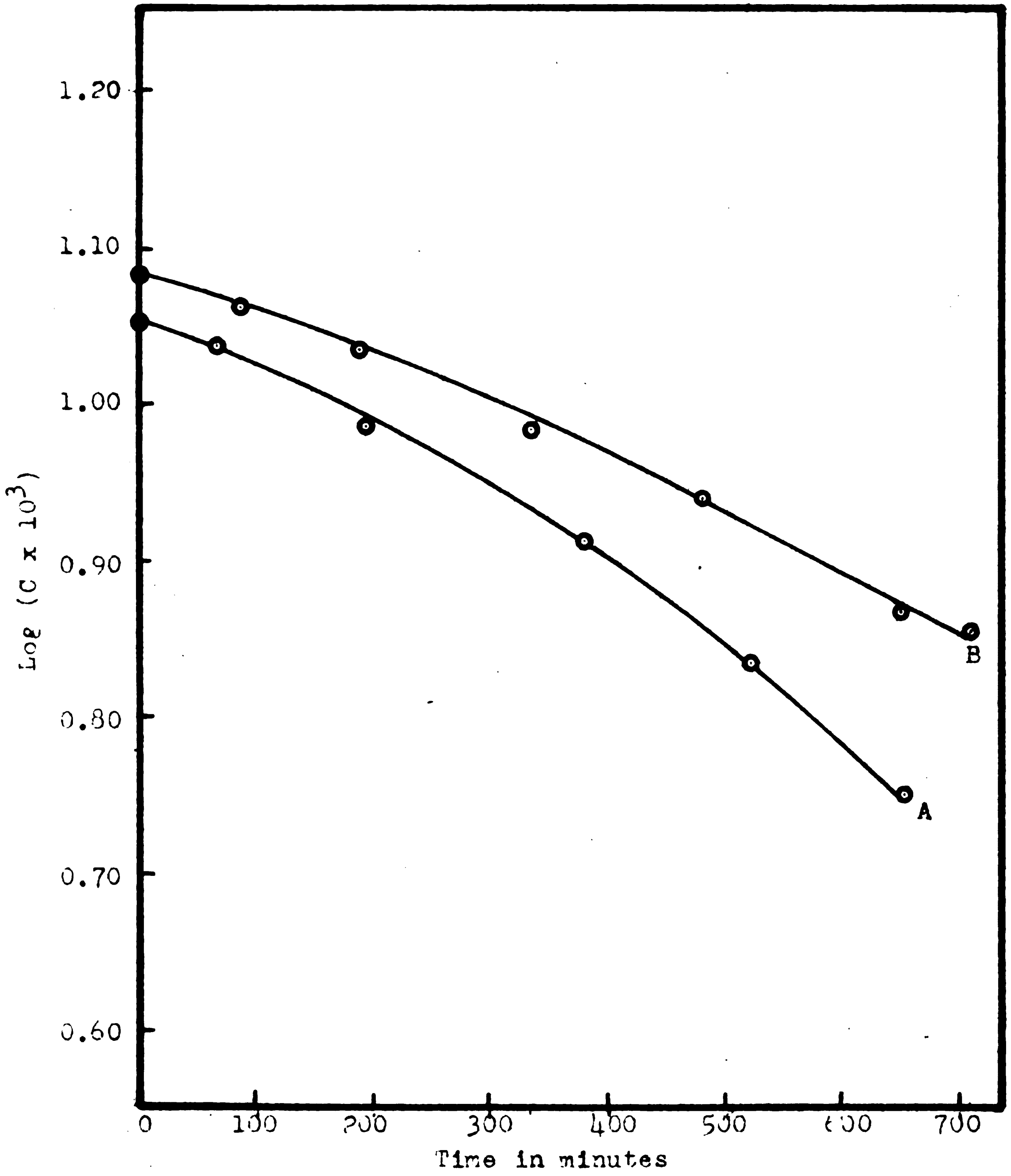


Figure XIII. Log peroxide concentration versus time for the decomposition of bis(5-nitro-2-thenoyl) peroxide in carbon tetrachloride at 75°. A-0.01 M peroxide in the presence of 0.20 M styrene. B-0.01 M peroxide in the presence of 0.20 M 3,4-dichlorostyrene

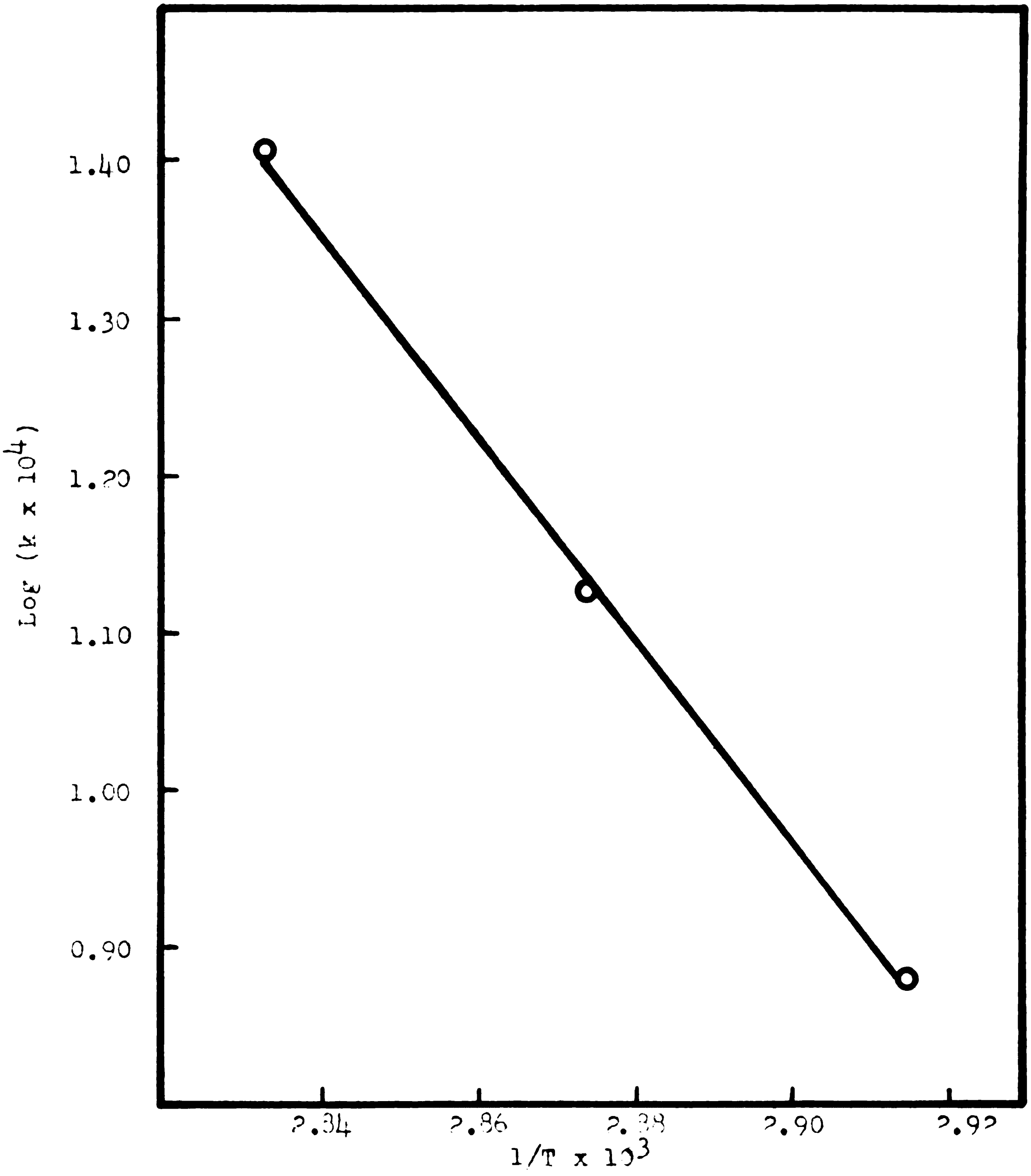


Figure **XIV.**. Log rate constant versus reciprocal of absolute temperature for the decomposition of bis (2-thenoyl) peroxide in carbon tetrachloride in the presence of 0.20 M 3,4-dichlorostyrene

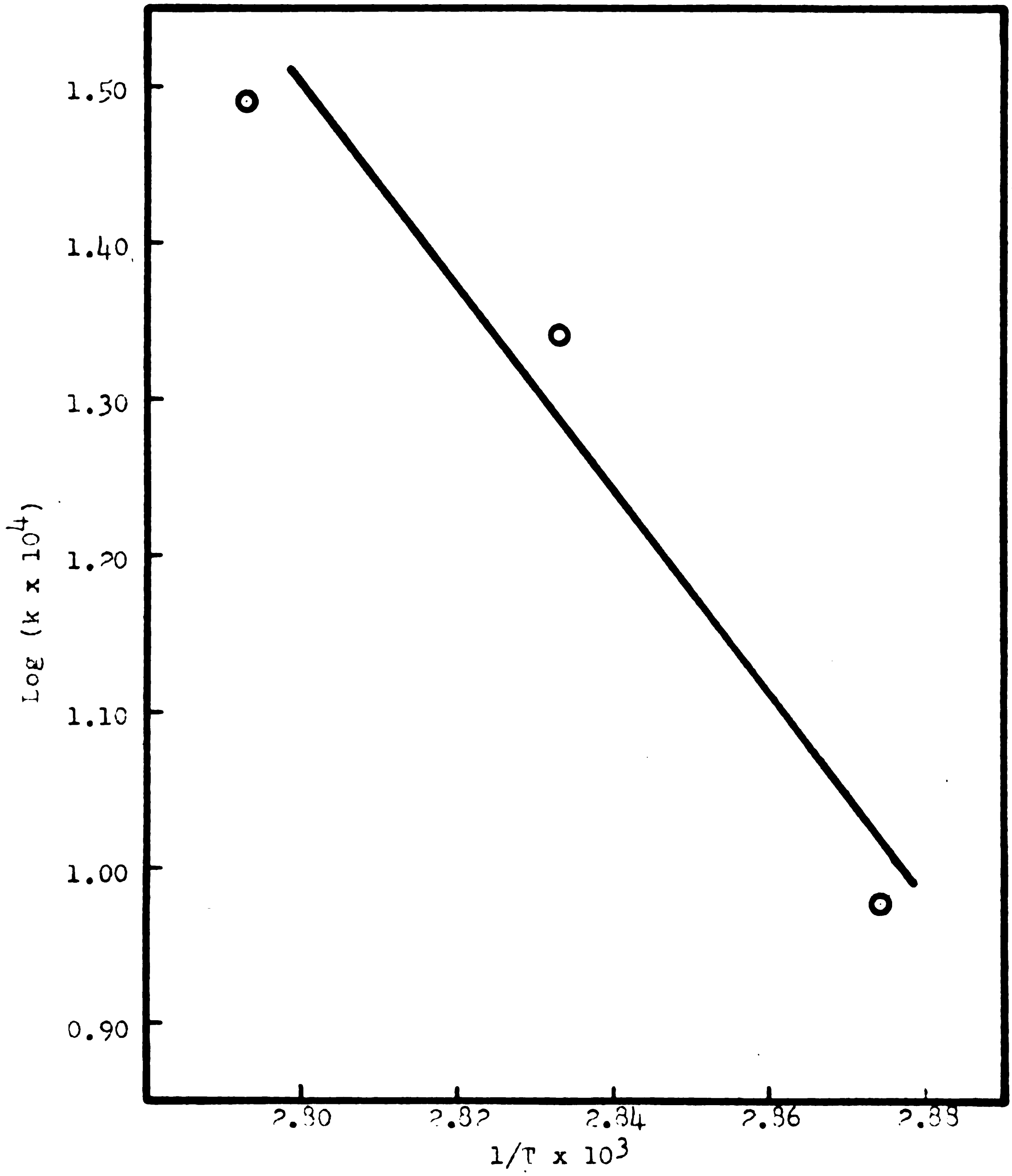


Figure **XV.** Log rate constant versus reciprocal of absolute temperature for the decomposition of bis (5-bromo-2-thenoyl) peroxide in carbon tetrachloride in the presence of 0.20 M 3,4-dichlorostyrene

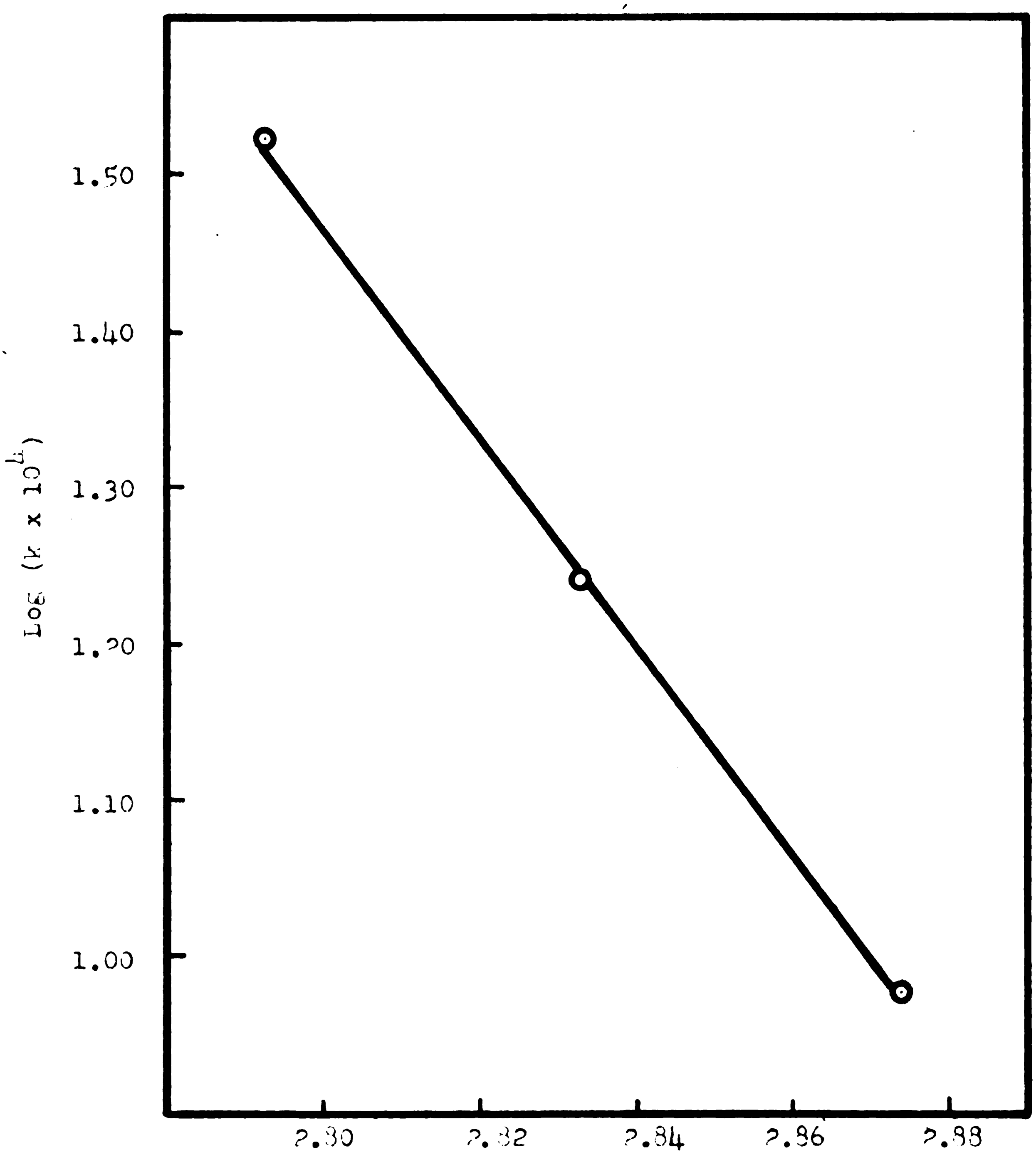


Figure **XVI.** Log rate constant versus reciprocal of absolute temperature for the decomposition of bis(5-chloro-2-thenoyl) peroxide in carbon tetrachloride in the presence of 0.20 M 3,4-dichlorostyrene

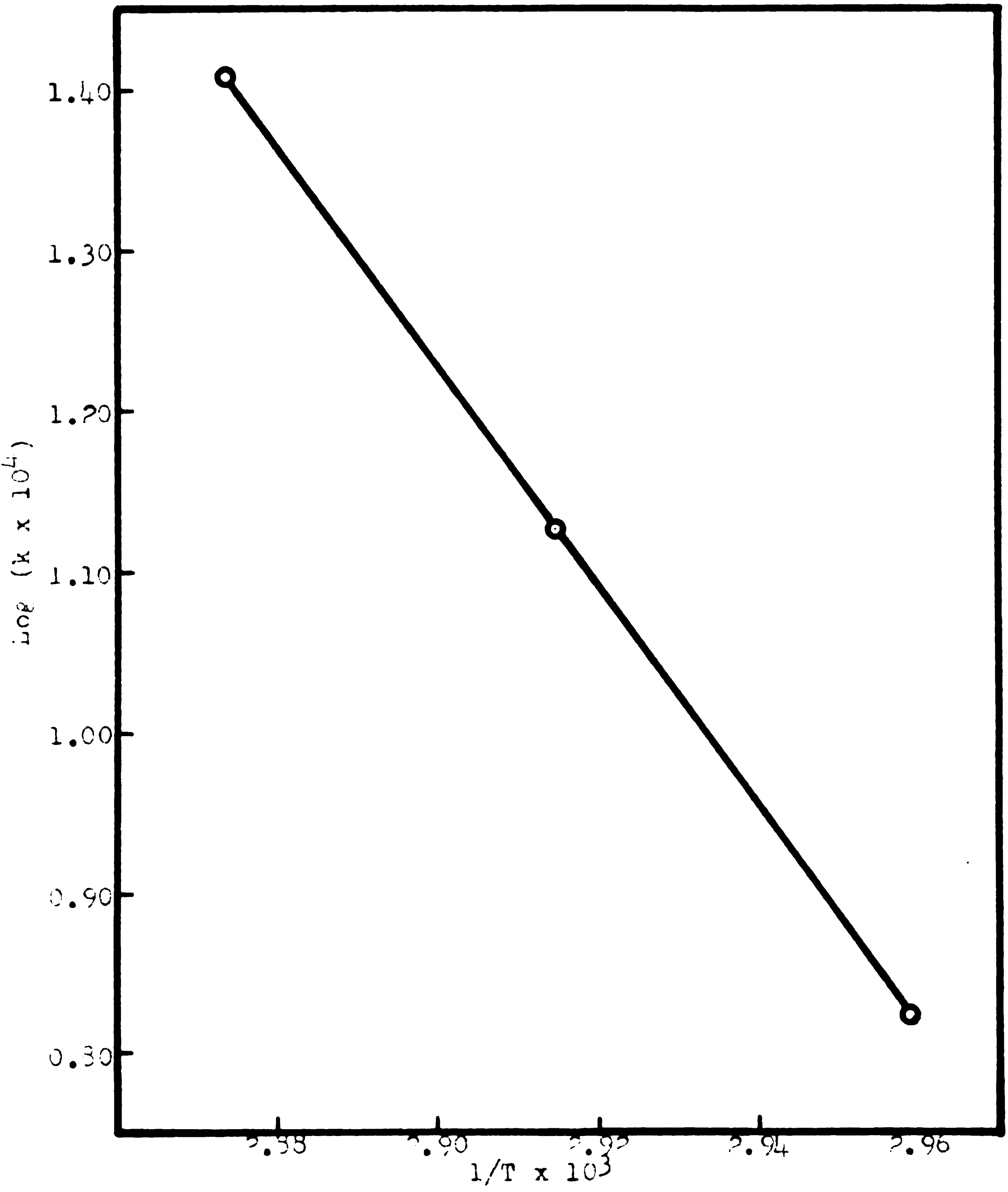


Figure **XVII.** Log rate constant versus reciprocal of absolute temperature for the decomposition of bis (5-methyl-2-thenoyl) peroxide in carbon tetrachloride in the presence of 0.20 M 3,4-dichlorostyrene

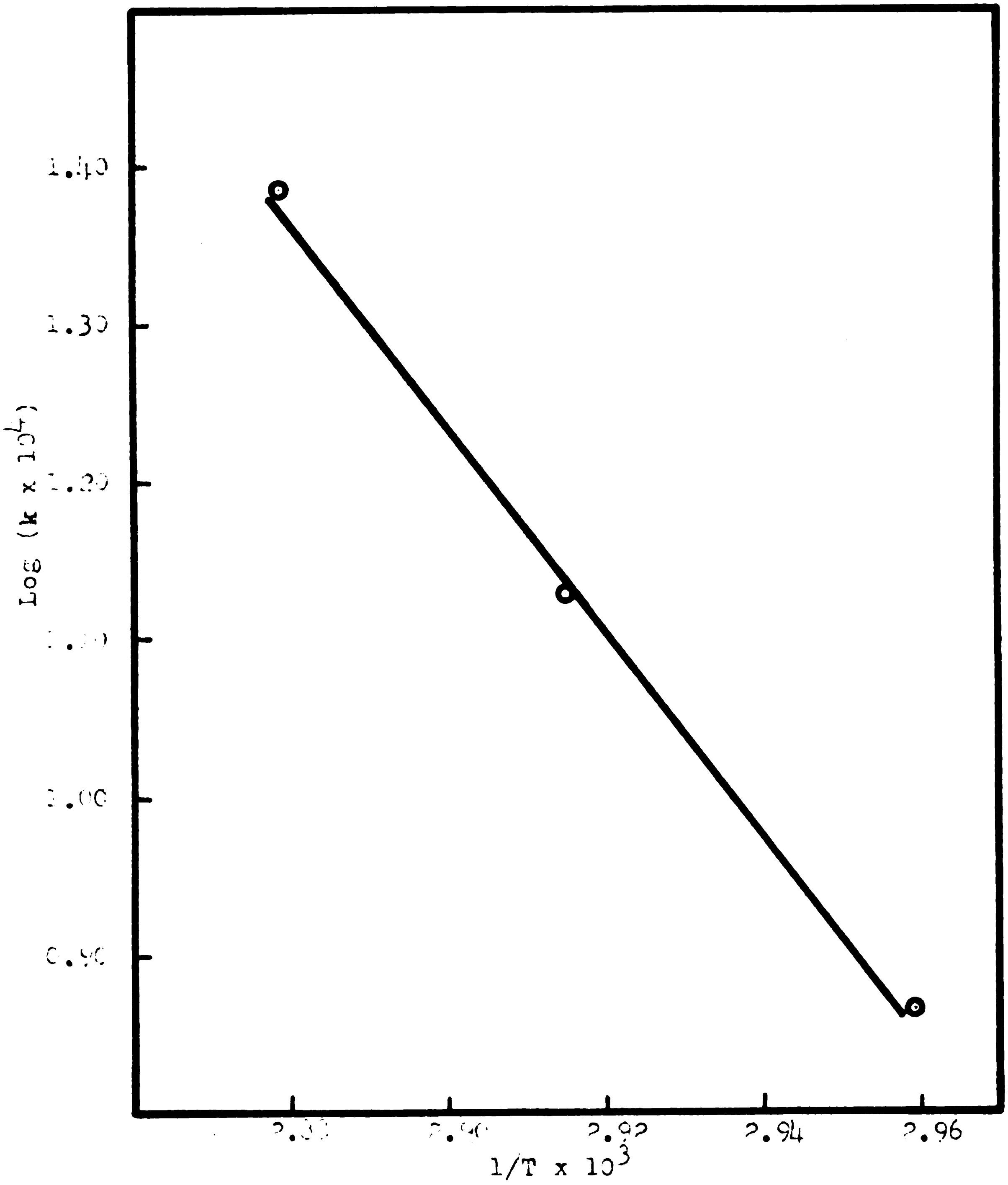


Figure XVIII. Log rate constant versus reciprocal of absolute temperature for the decomposition of bis (5-*t*-butyl-2-thenoyl) peroxide in carbon tetrachloride in the presence of 0.20 M 3,4-dichlorostyrene

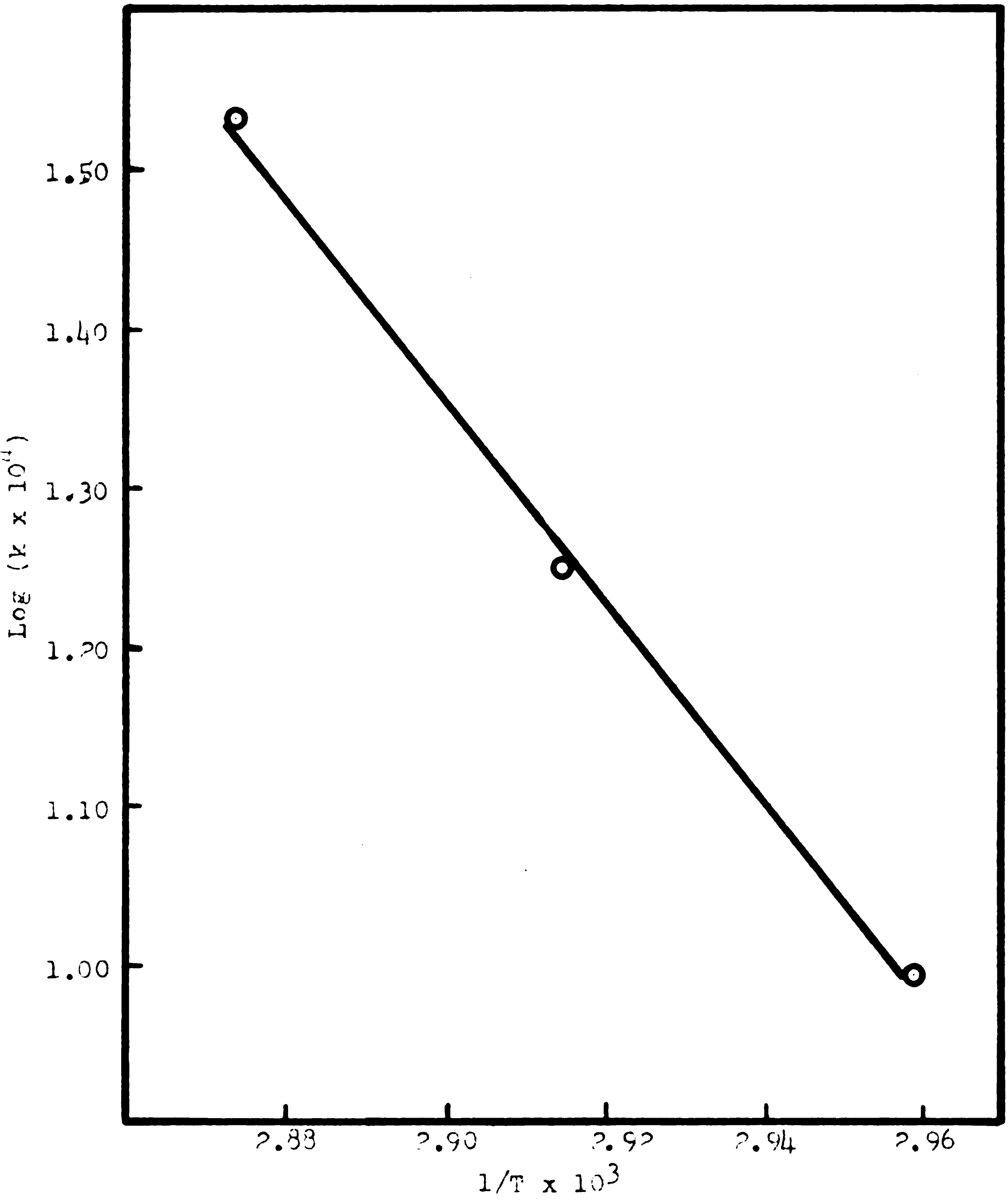


Figure XIX. - Log rate constant versus reciprocal of absolute temperature for the decomposition of bis (4-methyl-2-thenoyl) peroxide in carbon tetrachloride in the presence of 0.20 M 3,4-dichlorostyrene

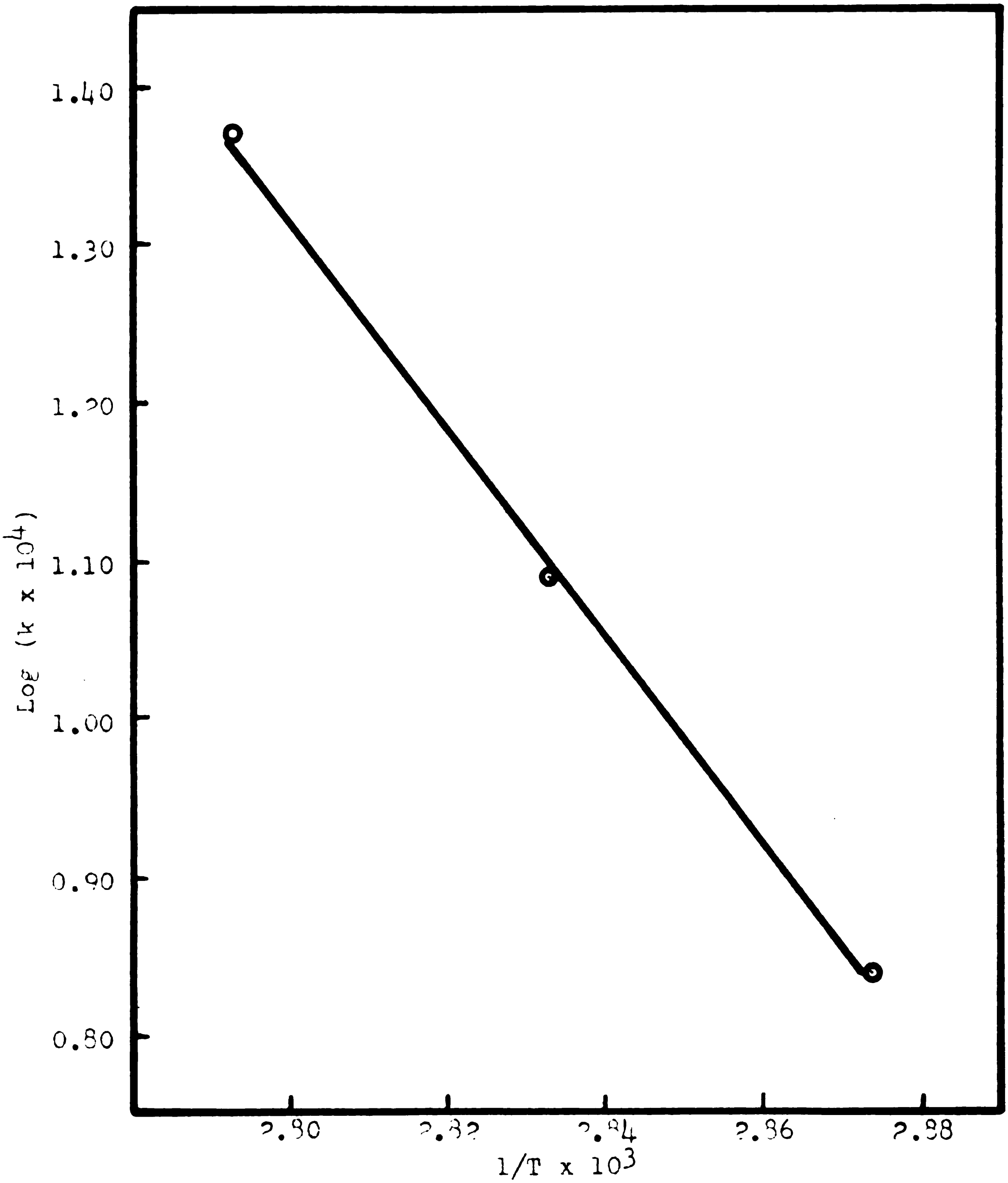


Figure XX. Log rate constant versus reciprocal of absolute temperature for the decomposition of bis (4-bromo-2-thenoyl) peroxide in carbon tetrachloride in the presence of 0.20 M 3,4-dichlorostyrene

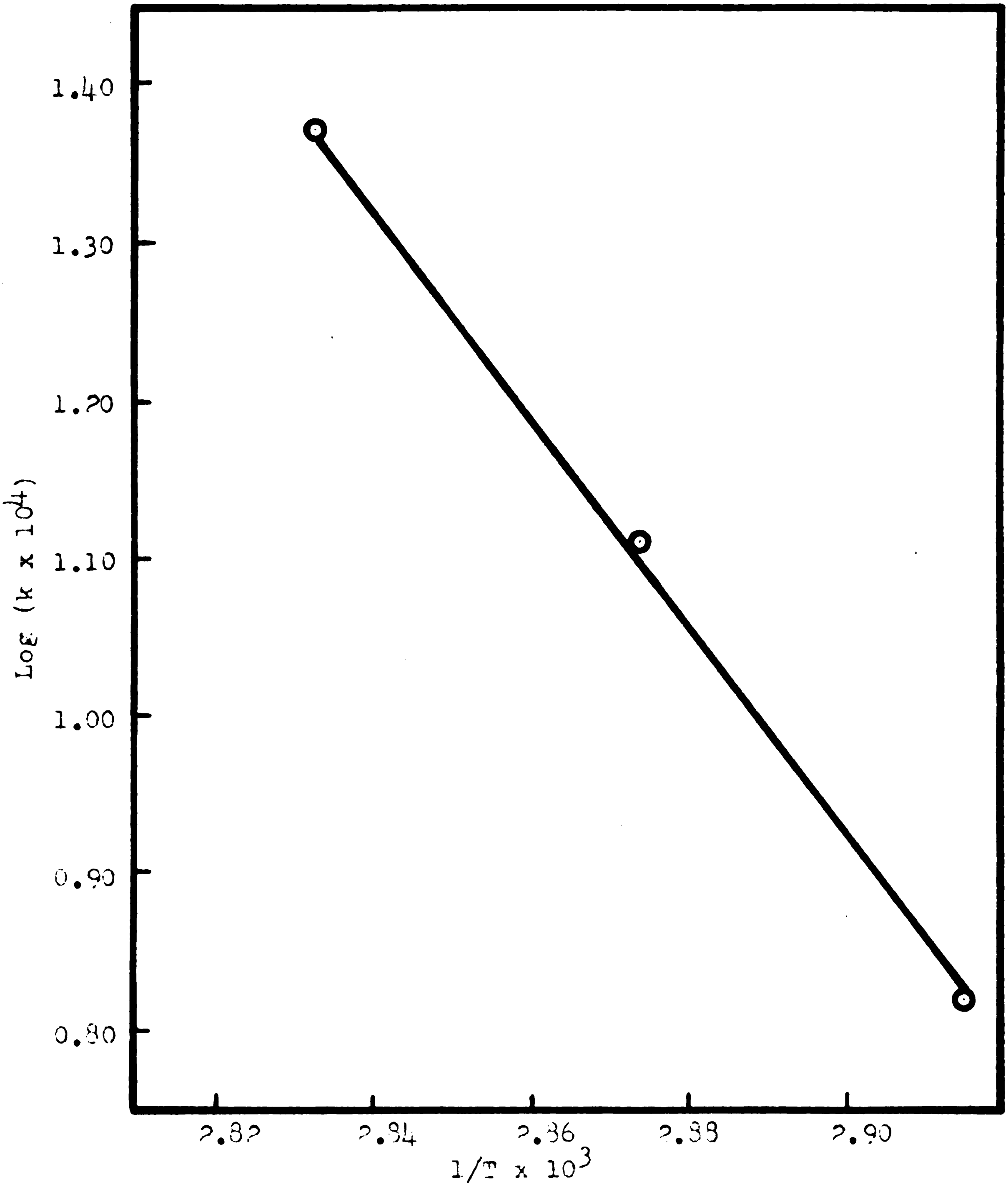


Figure XXI. Log rate constant versus reciprocal of absolute temperature for the decomposition of bis (3-thenoyl) peroxide in carbon tetrachloride in the presence of 0.20 M 3,4-dichlorostyrene

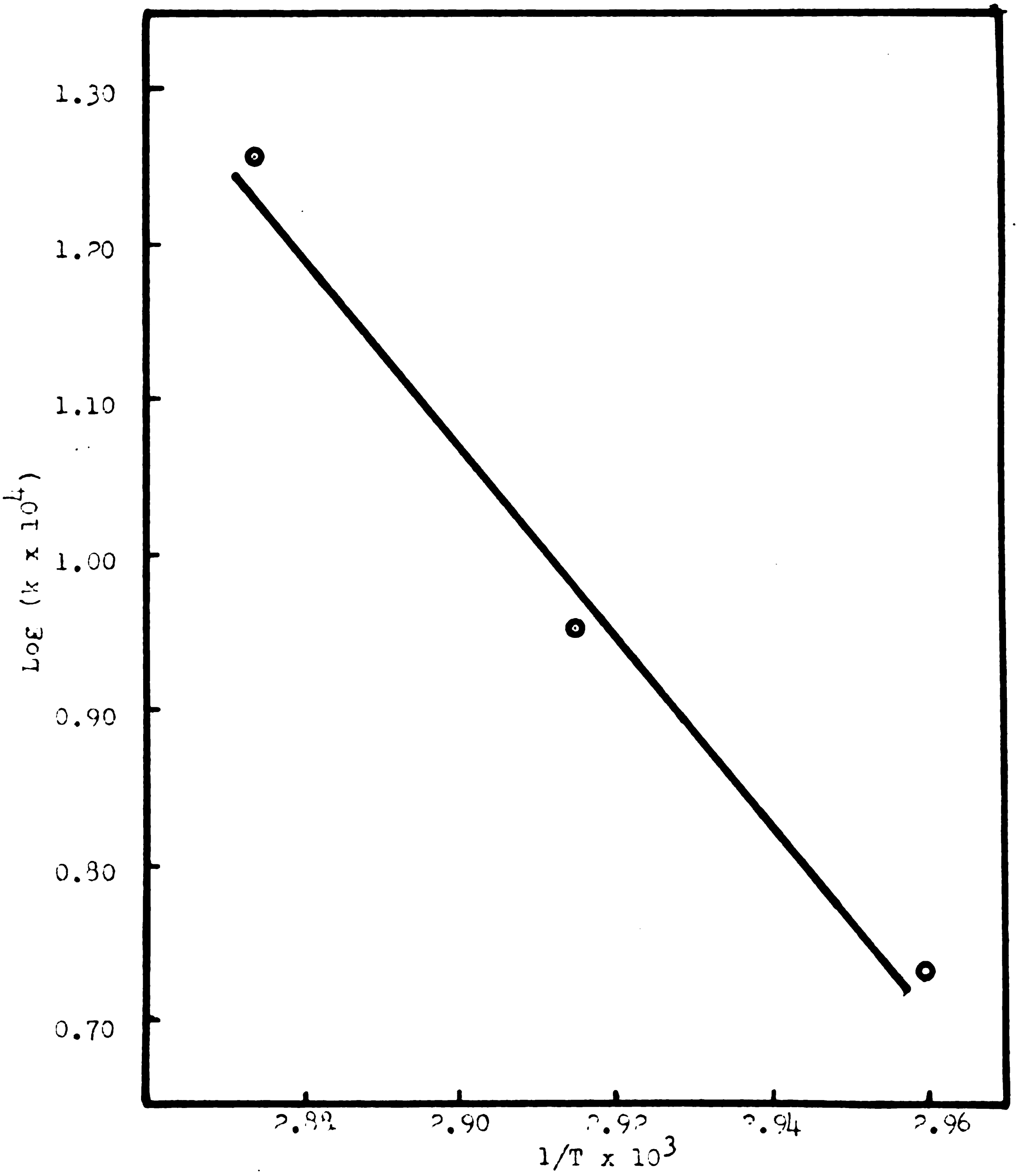


Figure XXII. Log rate constant versus reciprocal of absolute temperature for the decomposition of 5-methyl bis(2-thenoyl) peroxide in carbon tetrachloride in the presence of 0.20 M 3,4-dichlorostyrene

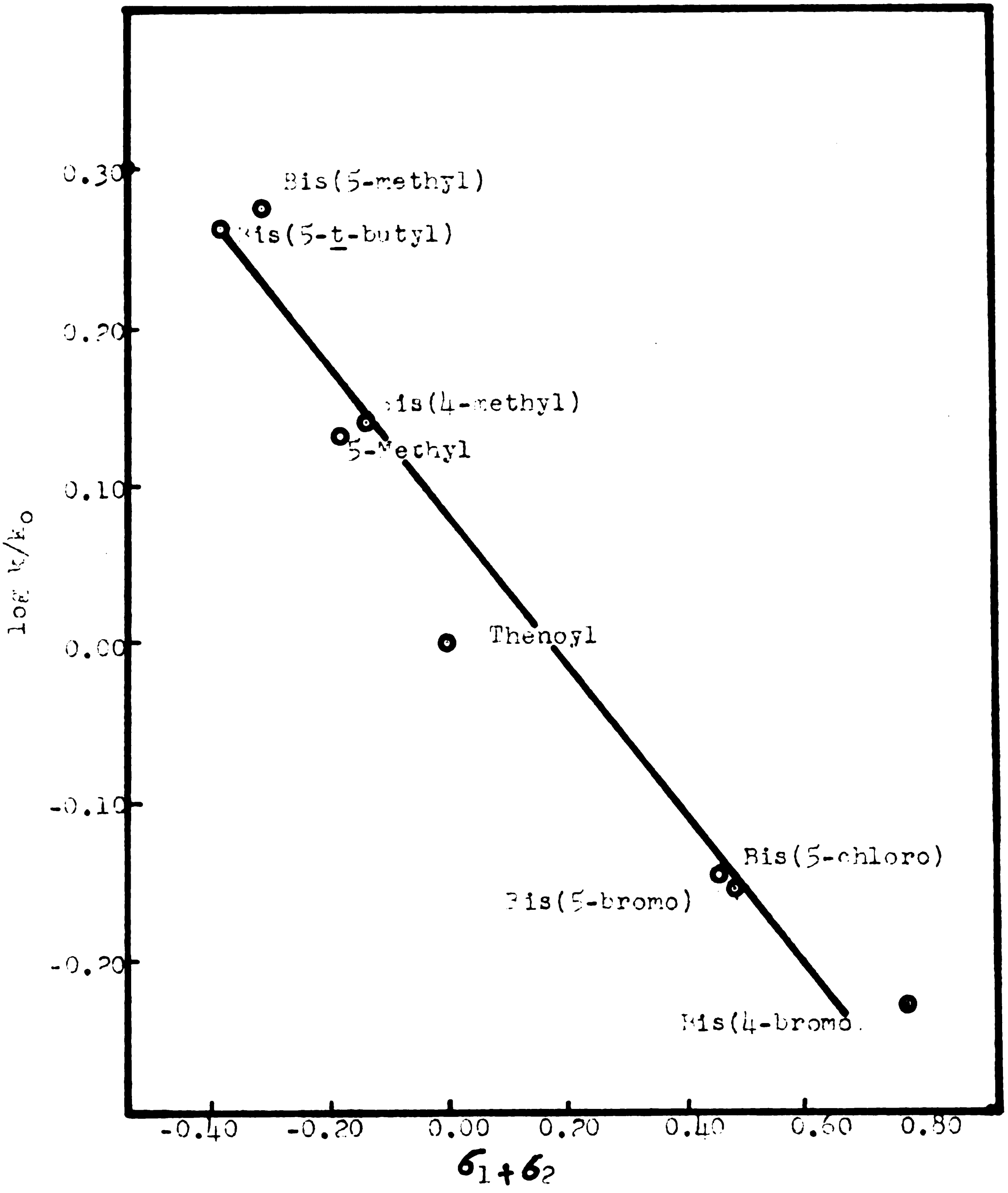


Figure XXIII. Plot of log k/k_0 versus $\sigma_1+\sigma_2$ for the decomposition of the bis(2-thenoyl) peroxides in carbon tetrachloride at 75°

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